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THORIUM-CARBON SYSTEM
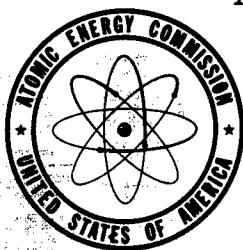
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THORIUM-CARBON SYSTEM[1]

I. ABSTRACT

A study of the thorium-carbon system has been made and a tentative phase diagram constructed from metallographic X-ray, and melting point data.

The existence of two compounds, ThC (4.92% carbon) and ThC_2 (9.38% carbon), has been verified. No conclusive evidence was found for any other compound. The monocarbide has a sodium chloride-type structure, and the lattice constant for this compound is shown to be 5.34 Å. This is considerably larger than the lattice constant previously reported for the monocarbide. It is shown that the lattice constant previously measured was that of a solid solution of thorium in thorium monocarbide. The lattice constant at room temperature for the monocarbide phase increases from 5.29 to 5.34 Å as the carbon content is increased from about 3.8 to 4.92%.

The monocarbide melts at 2625 $\pm$ 25° C and the dicarbide at 2655 $\pm$ 25° C. All compositions between thorium and the monocarbide show complete miscibility in the liquid state and in the solid state at elevated temperatures. However, an immiscibility gap in the solid solution area appears to extend from room temperature to just under the solidus line. The peak of this gap is at about 2% carbon and 1975° C. The compositions of the thorium-rich and carbon-rich solid solutions for this gap at room temperature are about 0.25% carbon and 3.8% carbon, respectively. The monocarbide and dicarbide also form a complete series of solid solutions at elevated temperatures but show little or no mutual solid solubility at room temperature. The dicarbide forms a eutectic with graphite containing approximately 12.6% carbon which melts at 2500 $\pm$ 35° C.

A method for measuring the electrical resistance at very high temperatures is given. Automatic recording and control instruments which can

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be used in conjunction with this method are described. This is essentially
a potentiometer method wherein the potential developed between two probes
which make contact with the test piece is balanced against a potential
developed across the secondary of a current transformer. The primary
of the current transformer is connected in series with the test piece.
The test piece, in the form of a bar is mounted between water-cooled
copper electrodes and is heated by passing a high 60 cycle current
through it. The change in resistance is measured directly.

Construction details of a furnace suitable for resistance heating
of test bars under vacuum or an inert atmosphere are given. This fur-
nace was used in determining melting points and in heating samples
whose change in resistance with temperature was measured up to approxi-
mately 2600° C.

The melting points of thorium-carbon compositions containing up
to 14% carbon were determined. The temperature dependence of the
electrical resistance of thorium and of a number of thorium-carbon
compositions was measured. Evidence indicating the existence of an
allotropic modification of thorium at temperatures above 1400° C is
presented.

II. INTRODUCTION

With the advent of atomic energy as a source of power and the fact
that thorium is one of the primary sources of nuclear fuels (1), the
physical properties of the metal and its alloys have been viewed with
renewed interest. Although many investigations have been conducted
on the preparation of the metal and on its physical properties, very
little work has been reported on thorium alloys.

Because of the reactivity of thorium it is difficult to prepare
metal free from impurities. Among the chief impurities found in the
metal are oxygen, nitrogen, and carbon. The extent of contamination
varies with the method of preparation. The effect of various impurities
on the physical properties of the metal is uncertain, but taken col-
lectively the effect of impurities is reflected by the wide variations
in the values reported in the literature for such properties as the
melting point, lattice constant, and specific resistivity of the metal (2).

The presence of impurities in thorium may also be expected to complicate any alloy studies in which thorium is the principal constituent. No reference has been found in the literature to any binary thorium system for which the thorium-rich end has been worked out. The only phase diagram involving thorium given by Hansen (3) in his critical review of binary alloys, is that of the thorium-aluminum system in which alloys containing up to approximately 75% thorium were studied. A search of the more recent literature revealed a rather thorough study of thorium-nickel alloys by Horn and Bassermann (4), but here again the thorium end of the phase diagram is incomplete. Probably the most detailed study of the thorium-rich end of a binary thorium system was the work done on the determination of the limits of solubility of carbon in thorium by Doig, Mallett and Saller as reported by Grenell and Saller (5) and by Jackson and Beaver (6).

No complete systematic study has been made of the thorium-carbon system. It is the purpose of the present work to extend the study of thorium-carbon alloys with the view of establishing a phase diagram for this system. Toward this end, metallographic, X-ray, melting point, and resistance-temperature studies were made.

III. REVIEW OF LITERATURE

The existence of a dicarbide of thorium was first reported by Troost (7) and later by Moissan and Etard (8). They prepared the carbide by reducing the oxide with carbon in an electric furnace at elevated temperatures. The structure of the dicarbide was studied by Stackelberg (9) and reported to be face-centered tetragonal with four molecules per unit cell with $a_0 = 5.85$ Å and $c_0 = 5.28$ Å. The melting point of the dicarbide was determined by Prescott and Hincke (10) by heating the compound in a graphite tube furnace to 2500° C. At this temperature fusion was observed to take place. Researchers at Battelle Memorial Institute (11) made X-ray studies of alloys formed in the process of determining the oxygen content of thorium metal by a vacuum-fusion method and reported the following phases: a monocarbide with a face-centered cubic structure of the sodium chloride type with $a_0 = 5.29$ Å, a dicarbide with a body-centered tetragonal structure with two molecules per unit cell with $a_0 = 4.14$ Å and $c_0 = 5.28$ Å, and slight evidence of a third face-centered cubic phase believed to be of the CaF_2 type with $a_0 = 5.85$ Å. The lattice constants for the dicarbide

are in close agreement with those reported by Stackelberg if referred to the same unit cell.

Baenziger (12) of this laboratory carried out X-ray-powder diffraction studies on alloys prepared by Treick and identified the compound ThC_2 for which he proposed an orthorhombic lattice with $a_o = 8.26$ Å, $b_o = 10.52$ Å and $c_o = 4.22$ Å and eight molecules per unit cell. On this basis he was able to account for all the lines obtained on X-ray powder diffraction diagrams. A second phase, believed to be the monocarbide, with a sodium chloride type structure with $a_o = 5.28_4$ Å was also identified. The metal is also face-centered cubic with the cubic closest packed copper-type structure. Baenziger reported the best value for the lattice constant for the pure metal to be 5.075_6 Å.

Considerable work has been done on the determination of the solid solubility of carbon in thorium at various temperatures. From X-ray diffraction studies of samples quenched from approximately 1950° C, Baenziger and Treick concluded that the maximum solubility of carbon in thorium at this temperature is approximately 0.7%. Researchers at Battelle Memorial Institute (5), (6) have studied the solubility of carbon in thorium by X-ray and metallographic methods and report the solubility to be approximately 0.1% at 900° C, 0.5% at 1050° C and somewhat higher at 1100° C. Hardness measurements were also made on samples quenched in water from temperatures up to 1400° C. Curves of Brinell-hardness number versus quenching temperatures for these samples show a sharp increase in slope at temperatures of 600 to 900° C. The samples having the highest hardness value at near room temperature gave a change in slope at correspondingly higher temperatures. This was interpreted to indicate that impurities begin to dissolve in low carbon thorium at about 650° C. Differential thermal analyses, using nickel as the reference test piece, gave curves for the temperature difference versus temperature of the thorium test piece which showed a small but definite break in the temperature range 650 to 750° C for low carbon thorium and one at 800° C for a specimen with higher carbon content. These data were also interpreted to indicate extensive changes in solid solubility in the temperature range given.

IV. SOURCE OF MATERIALS

Massive thorium of high purity and spectrographically pure graphite in powder form were made available by the Ames Laboratory for this in-

vestigation. In many of the experiments it was necessary to use finely divided thorium metal powder. The metal powder was prepared from cast metal by heating the metal in a hydrogen atmosphere to form a hydride powder which was then decomposed to give metal powder (13).

A. Preparation of Thorium Metal Powder

The steps used in preparing thorium metal powder may be outlined as follows:

1. Formation of the dihydride by heating the massive metal in a hydrogen atmosphere at 600° C.

2. Further reaction of the dihydride with hydrogen at 325 to 200° C to form a higher hydride.

3. Decomposition of the higher hydride by reheating the charge to 500° C under one atmosphere hydrogen pressure.

4. Further decomposition of the hydride by heating to 700° C under reduced pressure to give a rather finely divided metal powder.

A steel tube equipped with a water-cooled head was used to carry out the above reactions. The reaction tube containing several large pieces of metal was evacuated to a pressure of approximately one micron of mercury as the charge was gradually heated to about 250° C. The system was then partially filled with hydrogen and again pumped down to near one micron of mercury pressure, then again filled with hydrogen and the system thereafter maintained at a hydrogen pressure somewhat in excess of one atmosphere until the final decomposition of the hydride.

The initial reaction of hydrogen with the metal begins at about 400° C and once the reaction starts, hydrogen is taken up rapidly. It was therefore necessary to rapidly increase the flow of hydrogen into the system to maintain a pressure in excess of one atmosphere. The reaction is exothermic and there is a correspondingly rapid increase in temperature. The rate of the reaction soon subsides, and further heating is necessary to maintain a temperature of 600° C in order to bring about complete reaction. When the rate at which hydrogen was taken up became very slow, the furnace was shut off and the charge permitted to cool. At about 325° C the reaction again became quite rapid and reached

an optimum rate at about 275° C. This temperature was maintained until
the reaction became very slow, and the temperature was then gradually
decreased to about 200° C. During this reaction the charge breaks up
into a rather finely divided powder. This powder is pyrophoric and
ignites spontaneously on exposure to air at room temperature.

The charge was then reheated and hydrogen was rapidly given off at
one atmosphere of hydrogen pressure. The hydrogen was permitted to es-
cape through a vent. At 500° C the evolution of hydrogen ceased. The
hydrogen escape vent was closed and the vacuum pump started. The tem-
perature was gradually increased to approximately 700° C and pumping
continued until the pressure dropped to below 900 microns mercury pres-
sure. At this point the system was filled with helium and cooled to
room temperature.

At room temperature the water-cooled head on the steel reaction
tube was removed and several pieces of dry ice dropped into the tube.
This precaution was taken in order to prevent possible ignition of the
freshly prepared metal powder on sudden exposure to air. It was found
that most of the charge had been converted to a powder and some rather
loosely adhering lumps which could be broken up by means of a mortar
and pestle to pass a 30 mesh screen. The remainder of the charge con-
sisted of the center portion of several lumps of metal which had not been
converted to a powder, and of powder too coarse to pass a 30 mesh screen.

The minus 30 mesh powder was set aside for use in those experiments
in which the metal in powder form was required.

B. Chemical Analyses

Chemical analyses of the metal powder gave 0.090 and 0.042% of
carbon and nitrogen respectively. Metallic impurities accounted for
approximately another 0.12% of the metal. The metal was not analyzed
for oxygen content, however from results on cast metal the oxygen con-
tent in the metal powder was estimated to be about 0.10%.

Except for investigations conducted on the metal or on alloys of
very low carbon content the above impurities did not cause serious
complications. Some thorium-carbon alloys were prepared by heating

the fused metal in graphite crucibles at about 1800° C or above under vacuum. In this way the oxide and many of the other impurities were removed by volatilization.

The extent to which the metallic impurities are removed was checked by weighing the condensate from several test bars heated at about 2200° C for several hours. The bars were heated in a helium atmosphere in a resistance furnace. The furnace used is described on page 11. The condensate formed a fine loosely adhering powder on the water-cooled furnace cover. This was readily removed and weighed. The weight of the condensate was found to be approximately 0.10% of the metal used in making up the samples. This condensate is considerably more radioactive than the thorium metal indicating that decay products are also volatilized by this treatment.

V. APPARATUS AND METHODS

Due to the high melting point and reactivity of thorium-carbon compositions, furnaces suitable for their preparation and melting point determinations present some special problems. Thorium or thorium-carbon mixtures will react with or be contaminated by any of the commonly available refractory materials if heated in direct contact with the refractory at elevated temperatures, particularly at temperatures above 1800° C. Further, to prevent contamination by oxygen or nitrogen, it is necessary to carry out heating operations in an inert atmosphere such as helium or under vacuum.

A. Furnaces

Three types of furnaces were used in this investigation. An induction furnace was used to prepare fused and sintered alloys, a furnace for direct resistance heating of pressed powder compacts was used to determine melting points and in making resistance measurements, and a molybdenum tube furnace was used to presinter pressed powder compacts.

1. Induction furnace

The details of the induction furnace used is shown in Figure 1. The quartz tube has an inside diameter of approximately 4.5" and a length of 24". With a heater of 2.5" diameter by 4.75" long packed tightly in carbon black a rapid heating rate and a very slow cooling rate could be attained. A slow cooling rate was desirable in preparing alloys to be studied for phase regions existing at room temperature. With this furnace the temperature dropped from 2100 to 1400° C in approximately 30 minutes, from 1400 to 1000° C in approximately one hour, and then to near room temperature in about 10 hours. All alloys referred to as "furnace cooled" in the subsequent discussion will be alloys cooled at approximately this rate. This furnace will be referred to simply as an induction furnace.

2. Furnace for resistance heating

A furnace for direct resistance heating was designed and constructed. The details of the furnace are shown in Figure 2. In this furnace pre-sintered pressed powder compacts 0.25" x 0.25" x 4.0" were mounted between water-cooled copper electrodes and heated under vacuum or a helium atmosphere by passing a high 60 cycle alternating current through them. The refractory problem was obviated with this type of furnace.

The ends of the test bars were clamped between sets of heavy copper washers. One set was bolted firmly to one copper electrode while the other set was free to slide on top of the second copper electrode. At the latter electrode the test piece was held firmly between the two copper washers by means of two screws which did not extend through the under side of the bottom washer. In this way relatively free expansion and contraction of the test piece was provided for as the temperature of the test piece was varied.

It might be expected that some difficulty would arise due to arcing or heating between the sliding contact and the electrode. In order to prevent this from occurring the contact surfaces between the electrode and the bottom washer were polished to a smooth finish, and a small copper weight was placed on top of the two washers to press the surfaces together. Furthermore, the area between the washer and the electrode was large relative to other contact areas. Although complete contact

FURNACE SET-UP
FOR VACUUM HEATING

SIGHT GLASS

TO VACUUM

WATER OUTLET

WATER INLET

RUBBER GASKET

QUARTZ TUBE

WATER COOLED
INDUCTION COIL

CARBON BLACK
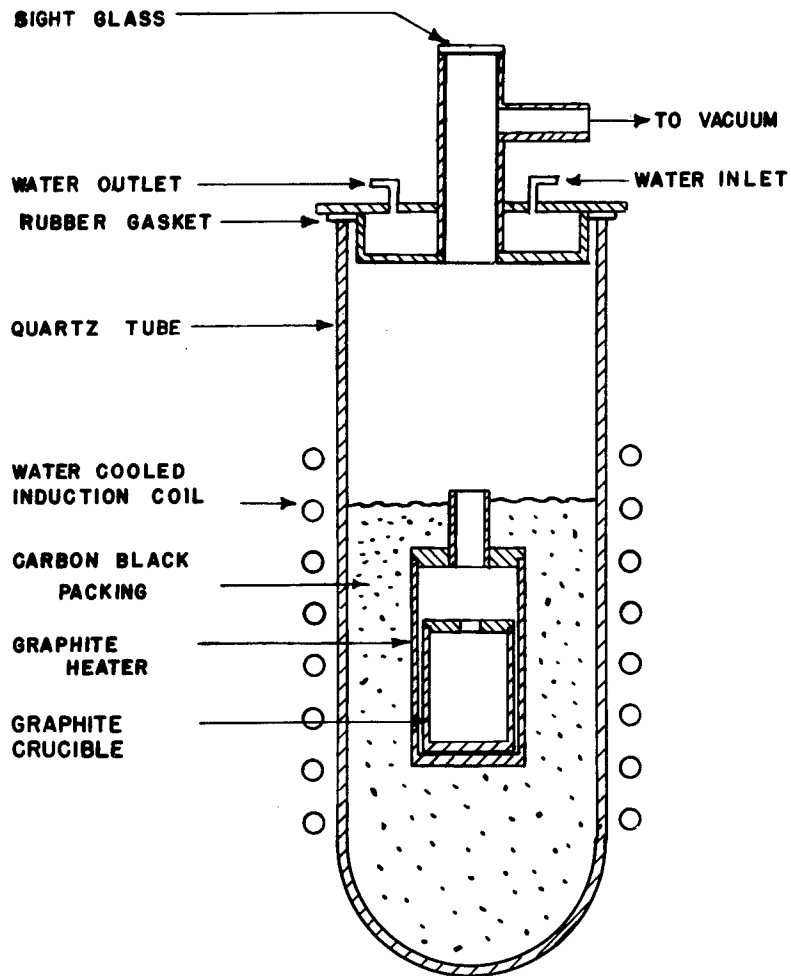PACKING

GRAPHITE
HEATER

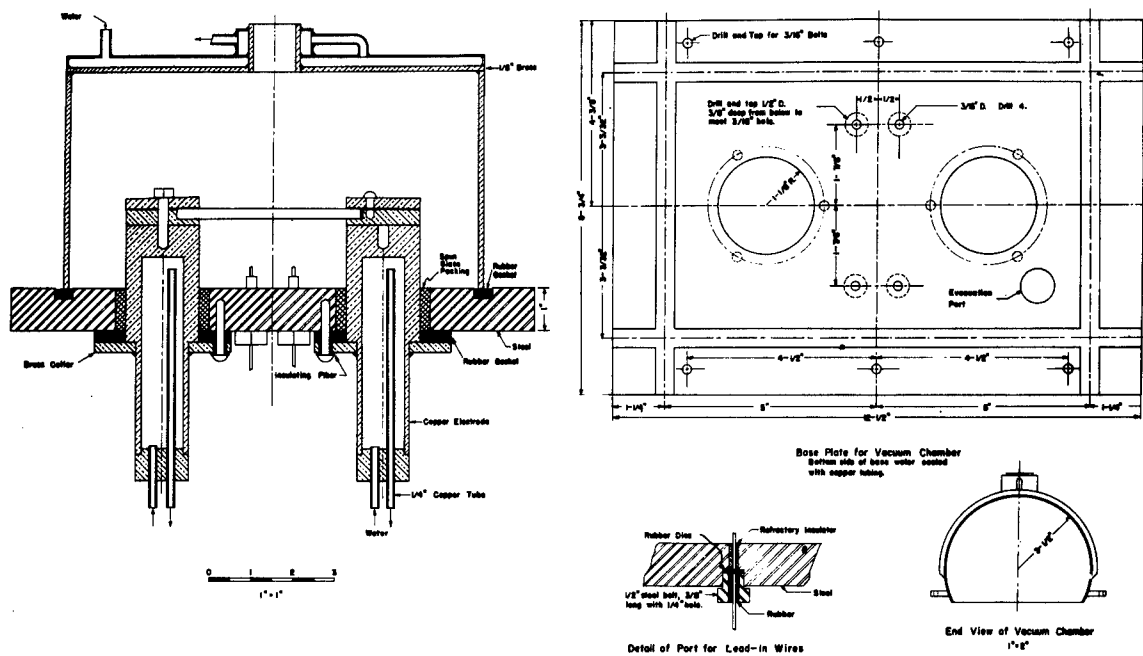GRAPHITE
CRUCIBLE

Fig. 1--Induction Furnace

Fig. 2--Construction Details of Resistance Furnace.

was not made over the entire area between the electrode and the washer, the resistance was still sufficiently small relative to the resistance of the test bar and the resistance between the bar and the washers, that no difficulty was experienced. However, it was sometimes necessary to retighten the screws which clamp the washers to the bar. In case the test piece was somewhat distorted, it was necessary to grind the ends or use thin copper shims between the washers and the test piece in order to bring about alignment and sufficient contact between the sliding washer and the electrode.

The test pieces were given a homogenizing anneal near their fusion point. At this temperature the pressure exerted by the small copper weight was sufficient to make the sliding contact settle down against the electrode surface and bring the full area into contact.

The furnace cover could be bolted firmly to the furnace base, and an inert gas pressure of above or below atmospheric could be maintained in the furnace without influx of air.

The usual procedure for filling the system with helium was to evacuate the furnace to 5 or 3 microns of mercury pressure, then to introduce helium into the furnace to a pressure of one atmosphere or less, followed by re-evacuation to near 5 microns mercury pressure, and finally to reintroduce helium to a pressure of somewhat above one atmosphere. The furnace when filled with helium was closed off from the rest of the apparatus. Expansion and contraction of the helium due to changes in furnace temperatures was provided for by means of a rubber balloon, of the type used on Fischer gas analysis apparatus, connected to the helium inlet to the furnace. In this way it was not necessary to maintain a constant flow of helium into the furnace, and the possibility of introducing reactive gases via the helium stream was eliminated.

The helium was purified by passing it over uranium shavings and then over thorium metal powder, both maintained at 500° C. The helium was first passed over the uranium shavings to remove oxygen and nitrogen. Any moisture present also reacts with the uranium shavings with the liberation of hydrogen. The helium was then passed over the thorium powder to remove the hydrogen and any unreacted oxygen or nitrogen. Although thorium powder alone might have been used, it does not react as rapidly as uranium with oxygen and nitrogen at this temperature.

In the subsequent discussion this furnace will be referred to simply as a resistance furnace.

3. Molybdenum tube furnace

A molybdenum tube furnace was used to presinter pressed powder compacts in order to render them sufficiently conductive to permit their being heated by means of a high current at voltages available in the resistance furnace, namely, at 8 volts or less.

The furnace was made from a molybdenum sheet 0.010" x 1.75" x 6". The sheet was rolled into a tube having an inside diameter of 0.5" and a length of 6". The seam, formed along the length of the tube, was spot welded at several points to give the tube rigidity and permanent shape. A molybdenum strip 0.010" thick by 0.5" wide was wrapped around each end of the tube and the free ends of each strip bolted to heavy copper connectors. This furnace could be mounted between the water-cooled electrodes of the resistance furnace previously described and heated electrically. A sketch of the furnace is shown in Figure 3.

B. Preparation of Alloys

Many of the alloys studied were prepared by powder metallurgy methods. Thorium and graphite powders of minus 30 mesh particle size were slightly moistened with carbon tetrachloride, then thoroughly mixed and pressed into compacts at 50,000 pounds per square inch pressure in suitable steel dies. The carbon tetrachloride was added to help prevent seggregation of the powder. The dies used are shown in Figure 4. The pressed compacts were then heated in an induction furnace in graphite crucibles or mounted between water-cooled copper electrodes and resistance heated by a high electric current.

Alloys were also prepared by heating molten thorium metal in contact with graphite at various temperatures for 10 to 30 minutes. By this method the melt takes up its equilibrium content of carbon at the particular temperature. Any excess carbon which diffuses through the solid carbide layer which forms between the melt and the carbon, precipitates at the solid-liquid interface, or simply contributes to the growth of the solid carbide layer. The center portion of each billet was analyzed for carbon content. Temperature-composition points on the liquidus curve of the phase diagram for carbon contents of 0.19 to 2.2% were determined in this manner.

6"

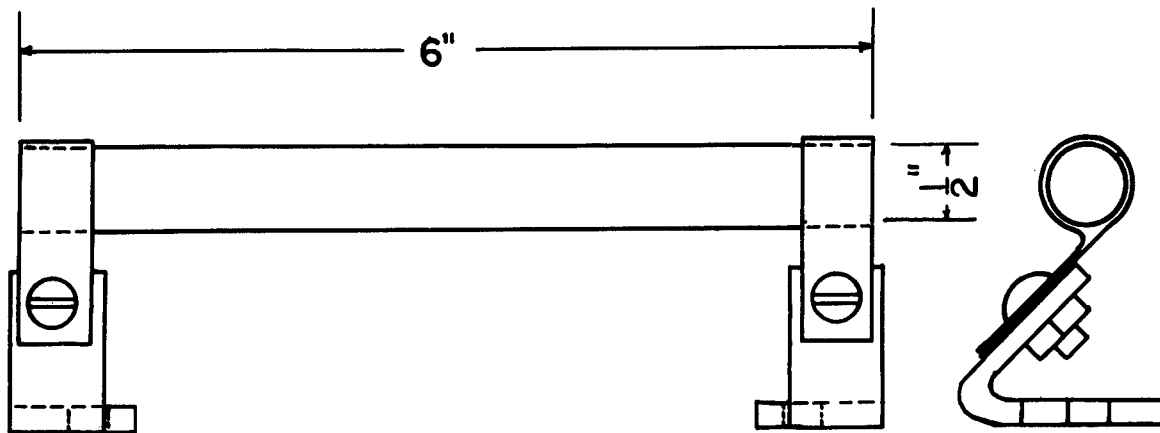$\frac{1}{2}$"

Fig. 3--Sketch of Molybdenum Tube Furnace

a

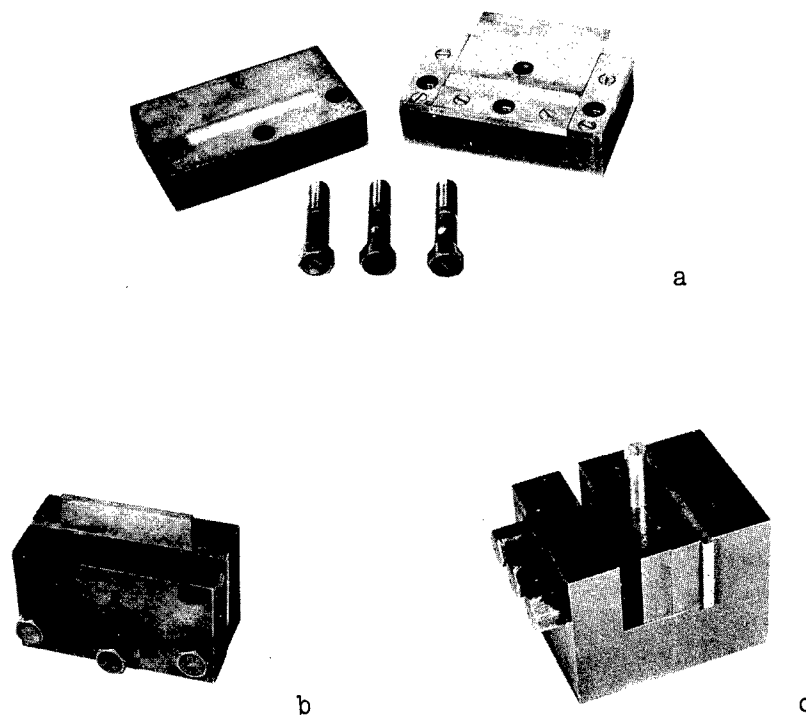b   c

Fig. 4--Steel Dies for Pressing Powder Compacts (a) - Bar die loaded
with powder, and (b) - Assembled die ready to be pressed. (c) - Die
for pressing 0.5" diameter billets.

C. Determination of Melting Points

Melting points of a series of alloys containing up to 14% carbon were determined by Pirani and Alterthum's (14) method which consists of heating a sample in the form of a bar by passing an electric current through it and observing the melting temperature by means of an optical pyrometer focused on a small hole or cavity in the bar. In this investigation, mixtures of metal and graphite powders were pressed into 0.25" x 0.25" x 4.0" bars at approximately 50,000 pounds per square inch in a suitable steel die. A small hole 0.039" in diameter and 0.150" deep, drilled with a long tapered point drill in the center of the bar normal to its long axis, was found to approximate black body conditions rather closely. Bars of low carbon content were presintered in a molybdenum tube furnace at approximately 1100° C for 5 to 10 minutes, and some of the bars containing more than 3% carbon were pre-sintered at approximately 1400° C in order to render them sufficiently conductive at 8 volts or less to be heated electrically. The sintered bars were then mounted between water-cooled copper electrodes and heated under vacuum or a helium atmosphere.

A Leeds and Northrup disappearing filament-type optical pyrometer was used in taking temperature readings. The pyrometer was calibrated against the melting points of pressed molybdenum and nickel bars by the above procedure. Two bars of molybdenum were observed to melt at 2590° and 2580° C. These readings were taken through a pyrex glass window and were then corrected for absorption by the glass window using the relation $I/T - I/T_a = -0.0000046$, developed by Foote, et al. (15), where T is the true absolute temperature and T_a is the apparent or observed absolute temperature. The corrected temperatures, 2628 and 2618° C respectively, are in good agreement with the literature value of $2623 \pm 10°$ C (16) for molybdenum. The melting point of nickel determined in the same way was found to be 1448° C, which is in fair agreement with the accepted value of 1452° C.

D. Preparation of Samples for Microscopic Examination

All alloys containing more than 4.0% carbon react rapidly with moisture and cannot be subjected to the usual wet polishing procedures. Well sintered 0.25" x 0.25" cross-section bars are completely disintegrated in eight hours of exposure to the atmosphere. The sintered

compacts are also very porous and extremely friable which add to the difficulty of obtaining well polished microstructures. The best results in polishing these samples were obtained by using fine grit emery paper either dry or impregnated with paraffin wax. Polishing on a cloth wheel using a carborundum suspension in a carbon tetrachloride-wax solution proved fairly satisfactory. Alloys containing less than 3.5% carbon can be wet polished by the usual procedures.

Thorium metal with less than 0.5% carbon can be polished and etched electrolytically with 50:50 glacial acetic and orthophosphoric acids. A current density of one ampere per square inch has been shown to be suitable for etching thorium (17). Quenched samples containing up to 3.5% carbon can be successfully etched with one part concentrated nitric acid to two parts methyl alcohol. The addition of 1 to 2% of a saturated aqueous solution of sodium fluosilicate improves the action of this etchant. A similar solution consisting of one part concentrated nitric acid to two parts of 95% ethyl alcohol, to which a small amount of sodium fluosilicate powder is added, can also be used for this purpose. Nitric acid can react rather violently with either ethyl or methyl alcohol and care should be exercised in working with these solutions. In one case, a solution of nitric acid and ethyl alcohol containing some sodium fluosilicate was observed to explode rather violently after standing in an open dish for a number of hours. Only a small amount of solution was involved and no damage was done other than that caused by the solution spattered on the ceiling. Thereafter the solutions were freshly prepared and then discarded after being used. These two etchants are quite slow in their action on pure metal, approximately 15 minutes being required to bring out the grain boundaries. The etched surface, however, is usually clean and free from films.

With alloys containing more than 3.5% carbon, the chief difficulty is to prevent overetching by air.

E. Apparatus for Resistance Measurements

The purpose for this apparatus was to measure the temperature dependence of the resistance of thorium and of thorium-carbon alloys. The resistance furnace described above was also used in these experiments. The test pieces on which resistance measurements were made had approximate dimensions of 0.25" x 0.25" x 4.0". These were heated in this furnace by passing a high 60 cycle current through them.

The method used in making resistance measurements is essentially a potentiometer method wherein the potential developed between two probes which make contact with the test piece is balanced against a potential developed by the secondary of a current transformer whose primary is in series with the test piece. A schematic diagram showing the various elements of the circuit is shown in Figure 5.

The secondary of the current transformer is firmly connected with heavy solderless copper connectors across a $1.0 \pm 0.15\%$ ohm manganin resistor. Special precautions were taken in making these connections since accidental opening of the secondary of a current transformer when a current is passing in the primary will result in the development of a very high voltage across the secondary endangering both equipment and operator. As shown in the circuit diagram, a 10.9 ohm resistor, a multitap resistor B, and slide wire C, all in series, are also connected across the current transformer in parallel with the one ohm resistor. The slide wire is 102 cm long and has a resistance of 0.00358 ohms/cm. The slide wire is used to find the balance point within close limits while the multitap resistor is used to pick off increments of resistance not exceeding the total resistance of the slide wire. The balance point is indicated by means of an alternating current galvanometer having a sensitivity of 0.06 microamperes per millimeter deflection and an internal resistance of 39.2 ohms.

From the resistance values given in the circuit diagram it is evident that at the balance point the following relation holds:

$$i_1 + i_2 = I/240$$

$$i_1 \times 1 = i_2 \times 14.52$$

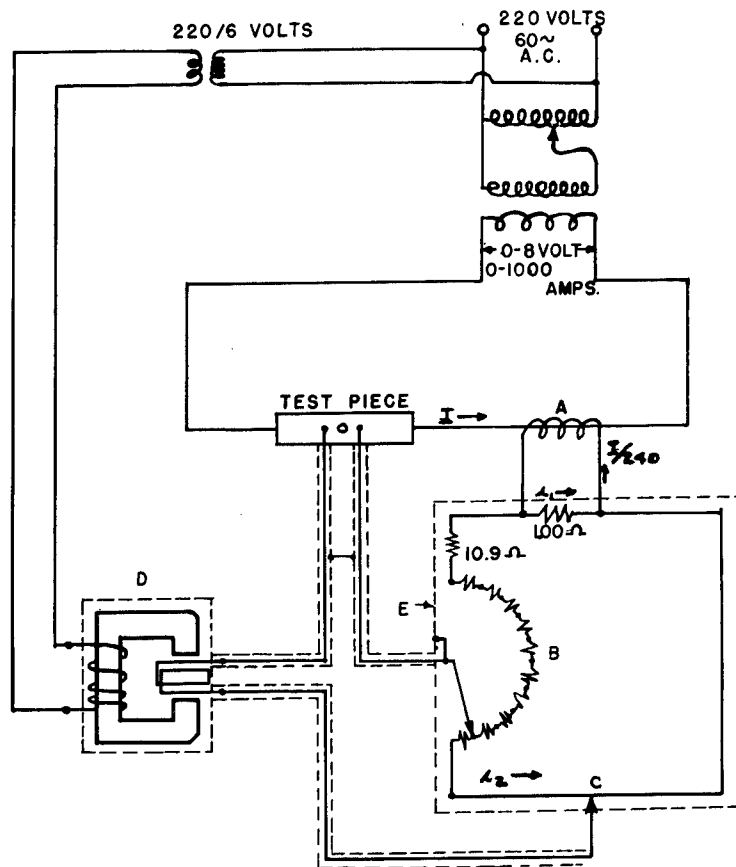and eliminating i_1 between these two equations gives

$$i_2 = I/240 \times 15.52.$$

Further,

$$IR_x = i_2 R_s = IR_s/3641$$

or

$$R_x = R_s/3641$$

RESISTANCE MEASURING CIRCUIT

A- CURRENT TRANSFORMER, RATIO 1200/5
B- MULTITAP SWITCH WITH 10 NONINDUCTIVE WOUND RESISTORS
   (0.326 Ω EACH) MADE FROM ONE CONTINUOUS PIECE OF
   #16 B & S MANGANIN WIRE.
C- SLIDE WIRE, #16 B & S MANGANIN WIRE, 0.00358 Ω/ CM.,
   102 CM. LONG.
D- A. C. GALVANOMETER
E- SHIELD

Fig. 5--Schematic Diagram of Circuit for Resistance Measurements.

where R_x is the resistance of the test piece between the two probes and R_s is the resistance between the contact on the multitap switch and the contact on the slide wire. The other quantities are as indicated on the circuit diagram.

A change in position of 1.0 cm on the slide wire corresponds to a change in R_x of 0.983×10^{-6} ohms.

1. Probable errors

In order to balance one alternating voltage against another it is necessary that the two voltages be of equal magnitude, 180° out of phase, and of identical wave form. These requirements could be attained rather closely by the above apparatus.

The current transformer secondary voltage was checked against the voltage developed across a number of test pieces over a wide range of current with an oscilloscope, and in no case could a difference in wave form or phase angle be detected.

The accuracy with which the change in resistance with temperature can be measured will be limited by the ability of the current transformer to maintain a constant current ratio and the phase shift introduced by the current transformer. The current transformer used was a commercial through-type switchboard-transformer with a current ratio of 1200/5. According to manufacturers' literature, a transformer of this type with a burden of one ohm and a 100% power factor, will have a ratio error well within 1.0% over a range of 10% to 100% of rated current, and the phase angle between the primary and secondary current over the above range will be 0.5° or less. A discussion of the characteristics of current transformers may be found in the "Standard Handbook for Electrical Engineers" (18).

In order to visualize quantitatively the error due to a small phase difference between two voltages to be balanced, consider a voltage B to be balanced by a variable voltage C which is 179° out of phase with B, and let A be the unbalanced component or the resultant of the two voltages, then A is given by

$$A^2 = B^2 + C^2 - 2BC \cos \theta$$

where Θ in this case is 179°. The change of A with respect to C is given by

$$\frac{dA}{dC} \cong (C - B \cos \Theta) / A.$$

At the point at which the galvanometer deflection is a minimum

$$C \cong B \cos \Theta \cong -0.99985 \ B$$

Therefore, the indicated voltage C required to balance B will be in error by less than 0.02% when the phase difference between B and C is 179°.

The sensitivity of the method will depend on the sensitivity of the galvanometer in detecting the extent of unbalance of the two voltages. As shown in Figure 5, the field coil of the galvanometer is energized through a 220/6 volt step-down transformer connected to the 208 volt supply. With test pieces of very low resistance, the high current transformer supplying current through the test piece is operating at near short circuit conditions. Under these conditions a large phase angle exists between the current through the galvanometer field coil and the current which flows through the suspended coil in the galvanometer. For ideal conditions the phase angle between the current in the field coil and the suspended coil is 180° or 0°. The sensitivity of the galvanometer approaches zero as this phase angle approaches 90°. The resistance of the thorium-carbon test bars used, had a sufficiently high resistance, and the galvanometer had sufficient sensitivity to permit detection of a minimum point without correcting this phase difference.

Potential contacts to the test piece were made by means of two 0.060" diameter thorium wires. These were bent in the shape of an "L", and the short end of each wire was ground to a point. These two points were fitted into two small depressions drilled approximately 1 cm. apart near the midpoint of the test bar. The other ends of the wires were fastened by means of screw clamps to leads brought up through the base of the furnace. Spring tension of the contact wires and the lead-in wires held the contact points against the test piece. The purpose for the depressions was to prevent the contact points from moving out of position during heating of the test piece. Thorium wires served to make contacts with test bars of high carbon content for resistance measurements at temperatures well above the melting point of thorium. On slowly heating to high temperatures, carbon from the test piece diffused

into the contact points raising their melting temperatures. This effect
and the high temperature gradient existing along the wire made it pos-
sible to use these contacts up to the melting temperature of all the
alloys studied. The contact wires were used many times, and the net
decrease in carbon content of the test bar due to diffusion was considered
negligible. New wires uncontaminated with carbon, however, were used
when tests on the pure metal were made. Small direct currents, due to
concentration gradients in the wires or due to connecting the thorium
wires to a dissimilar metal in the furnace, do not cause serious com-
plications in this method for measuring the resistance. The net effect
of a direct current component through the galvanometer would be a fuzzy
spotlight image. The same effect is produced with an alternating com-
ponent of current 90° out of phase with the current in the field coil.

In order to keep leakage currents and stray induced voltages to a
minimum, all connections to the measuring circuit and to the furnace con-
tacts were made through shielded cable. A sheet iron shield was placed
under the slide wire and galvanometer, and this in turn was connected
electrically to the steel frame supporting the furnace and to the steel
housing of the input transformer. One side of the input to the bal-
ancing circuit was grounded to the shield.

2. Automatic recording equipment

Resistance measurements with the manually operated apparatus were
tedious and time consuming. With an average heating rate of about
five degrees per minute, a heating and cooling run usually required
ten to sixteen hours. A much slower heating rate was desired. An
attempt was therefore made to adapt the above method to automatic record-
ing and control instruments.

A high speed direct current Brown Electronik recording potentiometer
was adapted to record changes in resistance. For this purpose, circuit
diagrams and manufacturer's literature (19), as well as other pertinent
information were obtained from the Brown Instrument Company. The changes
made in the input and measuring circuits of the instrument are shown in
Figure 6. The multiple pole double-throw swith shown in the circuit
diagram was installed to facilitate conversion of the instrument from an
alternating current potentiometer back to a standard direct current
potentiometer should it be desired to do so. When used as an alternating
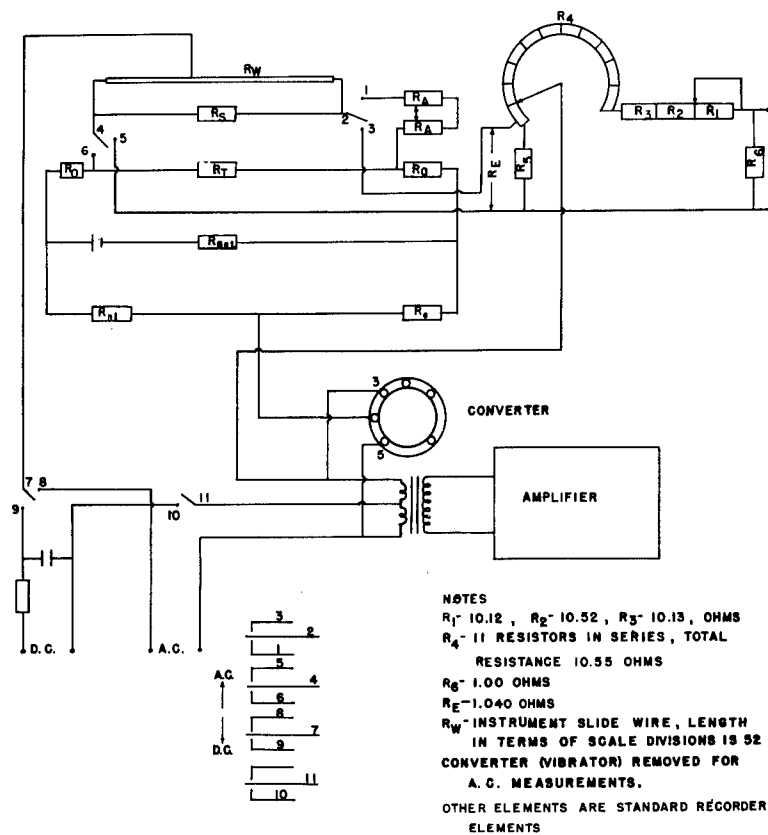
NOTES

R_1- 10.12 , R_2- 10.52 , R_3- 10.13 , OHMS

R_4- 11 RESISTORS IN SERIES , TOTAL
RESISTANCE 10.55 OHMS

R_6- 1.00 OHMS

R_E-1.040 OHMS

R_W- INSTRUMENT SLIDE WIRE , LENGTH
IN TERMS OF SCALE DIVISIONS IS 52

CONVERTER (VIBRATOR) REMOVED FOR
A. C. MEASUREMENTS.

OTHER ELEMENTS ARE STANDARD RECORDER
ELEMENTS

Fig. 6--Schematic Diagram for Input and Measuring Circuits of Automatic
Recorder.

current potentiometer, the instrument vibrator was removed. The multitap resistor shown was used for the same purpose as the multitap resistor used in the manually operated potentiometer, namely, to change the range of the instrument.

Other automatic controls and equipment used in conjunction with the recorder are shown schematically in Figure 7. As indicated in this diagram, the range of the automatic resistance recorder is changed by means of a small reversing motor which is connected to the shaft of the multitap resistor. The connection between the shaft of the motor and the shaft of the resistor is made through a stiff spring which serves to give a snap action to the movable contact. As the pen travel of the instrument reaches full scale, a small protruding arm fastened to the pen carriage trips a small "snap switch" which starts the motor in a clockwise direction. The motor drives the contact on the multitap resistor to the next point of higher potential or higher resistance. As soon as the change in position is made, the instrument pen moves rapidly down scale to its new balance point, the "snap switch" is released and the motor stops. The resistance between contacts on the multitap switch is approximately 3% less than the effective resistance of the slide wire, so the new balance point is above the zero point of the slide wire. A similar "snap switch" is mounted at the down scale end of the slide wire which starts the motor in the opposite direction. If the pen travels down scale, as is the case when the resistance of the test piece is decreasing, a similar sequence of operations take place when the pen reaches the end of the scale and the contact on the multitap resistor is moved to the next position of lower potential.

With a large phase angle between the supply voltage to the recorder and the voltage to the measuring or input circuit, the sensitivity of the instrument is quite low. To eliminate this decrease in sensitivity, a means for changing the phase angle of the supply voltage to the recorder was provided. Two autotransformers were connected in series across the main 208 volt supply with the series connection tied to ground or neutral. Each side of the 208 volt supply was 120 volts above ground with a phase angle of 120° between the two voltages. By taking the input voltage to the recorder from the two sliding contacts on the autotransformers, the supply voltage and voltage to the measuring circuit could be brought in phase. This was accomplished by observing the phase relation with an oscilloscope. The phase angle was corrected at the beginning of each run. Changes in phase angle during a run were not of sufficient magnitude to require correction.
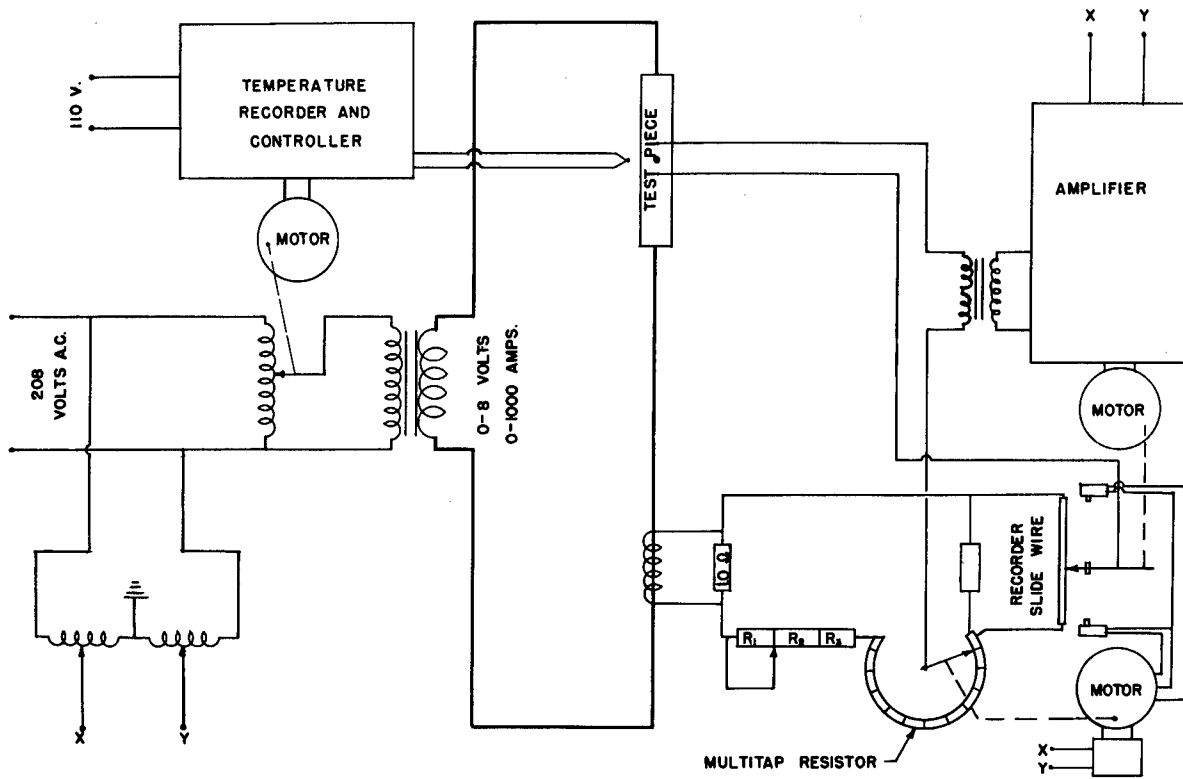
Fig. 7--Schematic Diagram of Automatic Recording Apparatus.

As the temperature of the test piece was increased, the voltage to the measuring circuit as well as the input voltage to the amplifier increased quite rapidly. In some cases it was therefore necessary to cut down the amplifier gain to prevent "hunting" at the balance point by the instrument.

A chromel-alumel thermocouple placed near the center of the test piece, but not in direct contact with it, was used in conjunction with a Brown automatic temperature recorder and program controller connected to the input autotransformer to regulate the increase or decrease of the temperature of the test piece. The temperature of the test piece could not be increased or decreased continuously, partly because of the limited number of turns on the autotransformer and partly because of the lag between the temperature of the thermocouple junction and the test piece. Under these conditions oscillating temperature regulation was obtained. To prevent this, the controller circuit was altered so that it served only to increase the input to the furnace on heating runs and decrease the input on cooling runs. In this way a step-wise control of the temperature was obtained. The steps varied between 10 and 25° C at temperatures above 750° C. Below this temperature the steps were somewhat larger.

With the test piece at 750° C or above, the indicated or recorded temperature of the thermocouple junction was found to be nearly a linear function of the temperature of the test piece. During either heating or cooling cycles, a number of temperature readings were taken with an optical pyrometer and the recorded temperature of the thermocouple junction noted for each reading. From these data a plot of thermocouple temperature versus test piece temperature was made and used to extrapolate intermediate temperatures.

The three resistors labeled R_1, R_2 and R_3 in Figure 7 were used to change the indicated resistance per division on the recorder scale. The scale of the recorder and the strip chart are divided into 50 equal divisions. This is the same scale and strip chart used with the standard 0-50 millivolt recorder. From the values of the resistances in the measuring circuit, as shown in Figure 6, and from the known length of the slide wire and scale, it can be shown that a change of one division on the slide wire corresponds to the changes in the measured resistance shown in Table I.

Table I

Equivalent Measured Resistance per Slide-Wire Division
With Various Resistors Short-Circuited

Resistors Short-Circuited	Measured Micro-ohms/per Scale Division
None	1.92
R_1	2.51
R_1, R_2	3.67
R_1, R_2, R_3	6.62

All leads to the input and measuring circuits of the recorder were shielded and one side of the input transformer was grounded to the shield.

The operation of the recorder was checked by making tests on a 200 ampere, 50 millivolt shunt. The shunt was connected across the copper electrodes in the furnace. The potential contacts and other connections were made to simulate actual operating conditions as closely as possible. With none of the resistors, R_1, R_2, and R_3, shorted out, recorder readings were taken as the current through the shunt was varied from 24 to 265 amperes. The recorder reading did not remain constant as would be expected with a constant resistance connected between the potential leads. The shunt resistance, as indicated by the recorder, varied from 250 to 257 micro-ohms. Similar readings were taken with the resistors, R_1, R_2, and R_3, shorted out in the sequence given in Table I. The indicated resistance over this range of measurements was found to vary from 250 to 267 micro-ohms. Assuming the true resistance to be 250 micro-ohms, the variation in the indicated resistance is approximately 6.8%. This was far too large a variation to be explained on the basis of changes in current ratio or actual changes in the shunt resistance. It was assumed that the observed increase in resistance with current was due to induced voltages. To check this interpretation, a copper bar with a uniform cross-section of 0.402 cm^2 and 10.2 cm long was next used to check the recorder. The copper bar was mounted in the furnace

and connections made in the manner shown in Figure 8a. A chromel-alumel thermocouple embedded in the sides of the bar was used to measure any increase in the temperature of the bar. The current through the test piece was varied from about 24 to 1100 amperes. The indicated resistance was found to be high by a factor of about two to four. The cause of this error was found to be due principally to induced voltage in the potential leads in the furnace. The leads were brought up through the one-inch steel plate furnace base as shown in Figure 8a. With the leads in this position, it is evident that the magnetic field set up by the two copper electrodes will induce an additive emf in the two leads. The leads were therefore rearranged as shown in Figure 8b. In this position the induced voltages in the two leads should oppose each other and tend to cancel. This was found to be the case and much more reasonable values were obtained for the measured resistance.

To further check the effect of induced voltages, the effect of variation in current on the zero point reading of the instrument was measured. The potential leads from the test piece to the recorder were disconnected and the input to the amplifier short circuited. The current through the copper bar was varied from about 24 to 1100 amperes and the change in zero point reading noted. As the current was increased from about 15 to 120 amperes, the observed increase in zero point reading was 0.6 divisions with R_1, R_2, and R_3 shorted out and approximately 1.8 divisions with none of the resistors shorted out. As the current was further increased from 120 to 1100 amperes, the zero point reading increased another 0.05 divisions with R_1, R_2, and R_3 shorted out and approximately 0.2 divisions with none of the resistors shorted out. These observations indicated pickup by the amplifier within the instrument as the voltage to the measuring circuit was increased.

Rather than try to correct this situation, it was decided to calibrate the instrument zero point and then correct the instrument readings. To do this, the potential leads to the recorder were reconnected and the probes or contacts to the test piece tied together in the furnace in order to include any variations due to induced voltages in the contact wires in the furnace and leads to the furnace. With R_1, R_2, and R_3 shorted out, the zero point reading increased 0.40 divisions, and with none of the resistors shorted out, it increased approximately 1.0 divisions, as the current was increased to 1100 amperes. Most of the increase took place as the current was increased to about 350 amperes. At higher currents the recorder readings remained essentially constant.
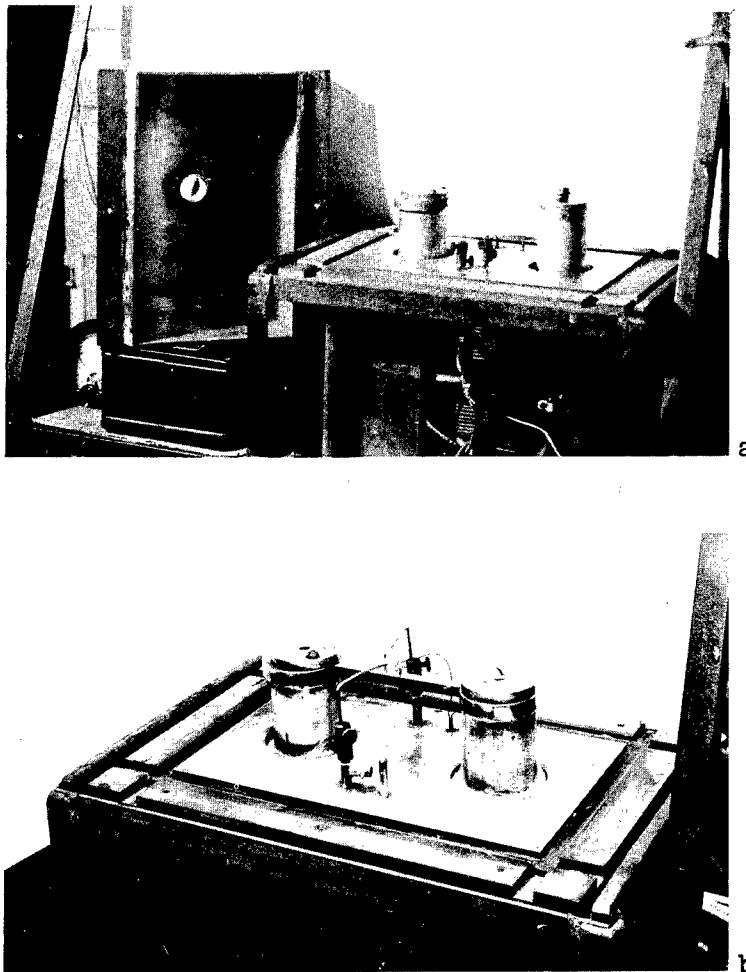
Fig. 8--Arrangement of Potential Contacts to Test Bar. (a) With lead-in wires symmetrically located on one side of the bar the induced emf in the wires is high. (b) With lead-in wires on opposite sides of the bar the effective induced emf is low.

The specific resistance of the copper bar, as calculated from the corrected recorder readings was found to be 1.83 micro-ohm-cm at 25° C. This agreed fairly well with the specific resistance, 1.81 micro-ohm-cm, as determined with a Kelvin bridge at 25° C.

The change in resistance with temperature in terms of scale divisions for most of the alloys studied varied from about 100 to 450 divisions. The error due to induced voltages is small when distributed over the range of measurements of any one run.

The effect of the difference in phase angle between the supply voltage to the instrument and the voltage to the measuring circuit was also measured over a wide range of current. A phase angle difference of up to approximately 20° produced no appreciable change in recorder reading. It did, however, reduce the sensitivity of the recorder. As the phase angle was increased further, there was a gradual increase in recorder reading, and the recorder became very sluggish in reaching a balance point. The recorder was considerably more sensitive to changes in phase angle when a large out-of-phase component existed in the input to the amplifier as was the case before the position of the leads into the furnace were changed.

A direct current voltage of 100 millivolts across the input of the amplifier had no effect on the recorder reading. The same voltage connected in series with the alternating current input likewise gave no change in recorder reading.

Since the sensitivity of the recorder is in part determined by the potential drop per unit length of slide wire and the input voltage, the sensitivity of this method is greatest at high temperatures.

The automatic recording and control apparatus is shown in Figure 9.

VI. EXPERIMENTAL RESULTS

A tentative phase diagram of the thorium-carbon system as constructed from metallographic, X-ray, and melting point data is shown in Figure 10.
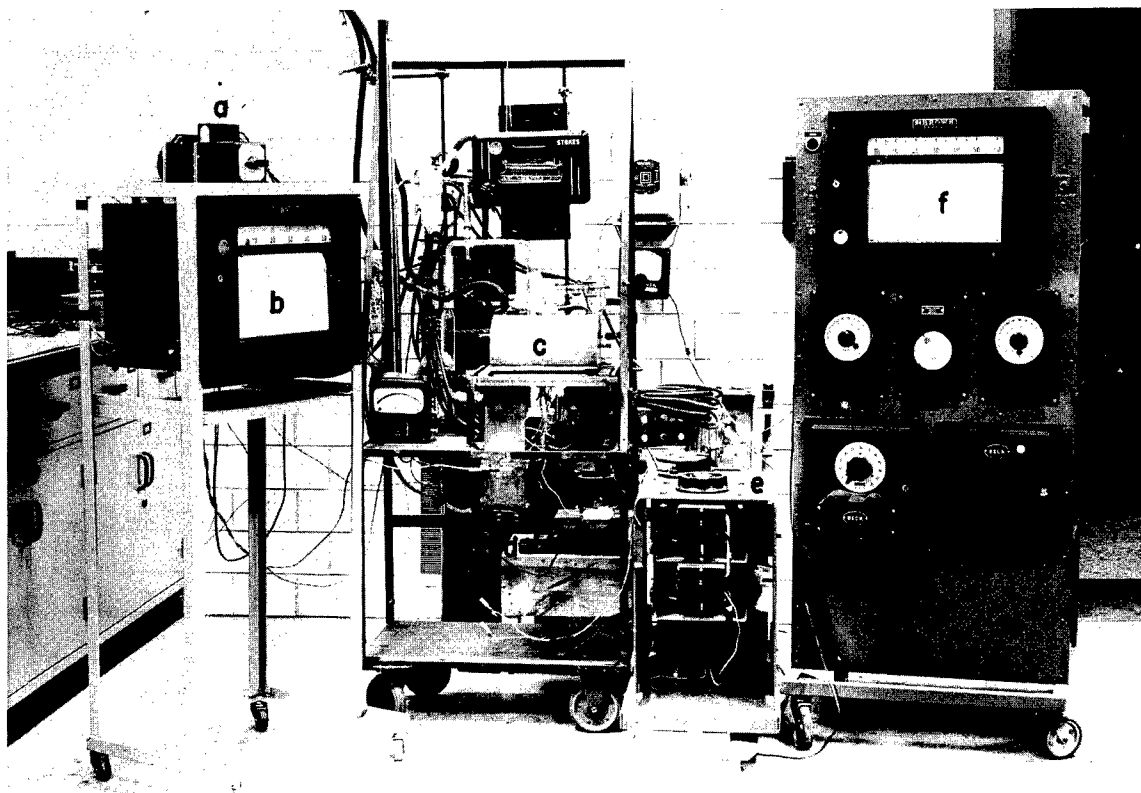
Fig. 9--Automatic Apparatus and Resistance Furnace. (a) Multitap switch and reversing motor, (b) Resistance recorder, (c) Resistance furnace, (d) Current transformer, (e) High current transformer, (f) Temperature recorder and controller.
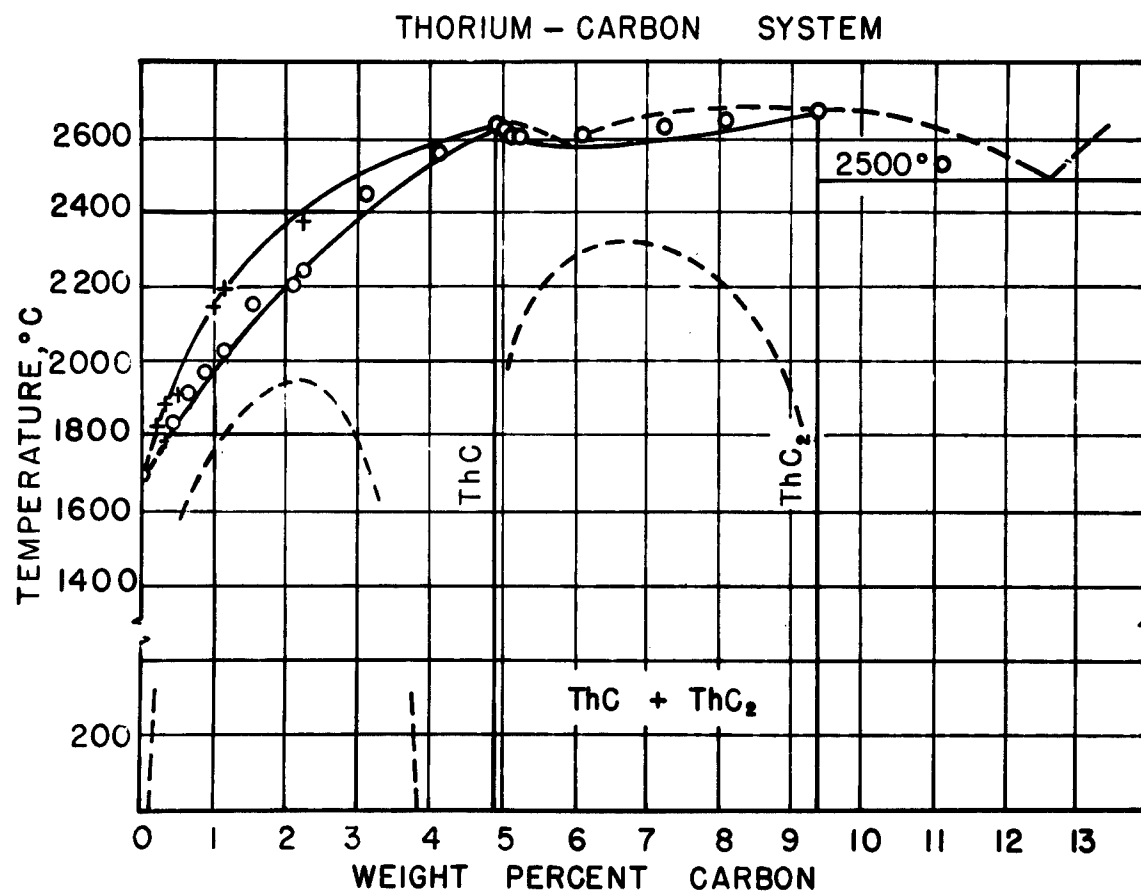
THORIUM — CARBON   SYSTEM

Fig. 10--Tentative Phase Diagram of the Thorium-Carbon System.

A. Diffusion Studies

The purpose of these studies was to obtain evidence for the one-phase regions in the thorium-carbon system at various temperatures. The diffusion bands, or layers formed by heating two components of a binary system in contact with each other will correspond, in the order of their occurrence, to the single-phase regions of the phase diagram at the temperature and pressure at which the diffusion bands are formed (20).

Evidence of the phases to be expected was obtained by observing the diffusion bands formed between the metal and carbon on heating thorium metal in a graphite crucible under vacuum in an induction furnace at 2100 to 2180° C for 22 minutes. Since the carbides of thorium are extremely brittle and friable, it was difficult to hold the carbide formed between the metal and crucible intact during polishing operations. To eliminate this difficulty, a small graphite rod was supported in the center of the melt and the diffusion bands formed around the graphite rod were firmly held in place by the surrounding metal. The structures of the bands obtained are shown in Figure 11. The curvature of the graphite rod is evident at the extreme left side and the direction of decreasing carbon content is from left to right. The banded structure of the innermost region of the first shell is characteristic of the structure of the dicarbide (see also Figure 12). The banded structure of the dicarbide, Figure 11, merges into a region with a lamellar structure extending up to the first demarcation line, indicating appreciable decrease in solid solubility of the monocarbide in the dicarbide on cooling to room temperature. The adjacent region shows a wide single-phase area of monocarbide partially darkened by the action of atmospheric moisture. This region gradually merges into an area showing a spheroidized precipitate of thorium, and with decreasing carbon content into a region showing a lamellar structure consisting of nearly equal amounts of the monocarbide phase and thorium, and finally to an area of monocarbide phase in a thorium matrix. The thorium phase and the monocarbide phase are both solid solution phases.

This interpretation was substantiated by X-ray analyses and micro-hardness measurements. The dark outer layer, including the dicarbide and the darkened region of the monocarbide, is readily removed from the rest of the sample. X-ray analyses of this material showed only two phases present, the monocarbide with a lattice constant of 5.33$_8$ Å and thorium dicarbide. Microhardness tests of the light and dark phases on
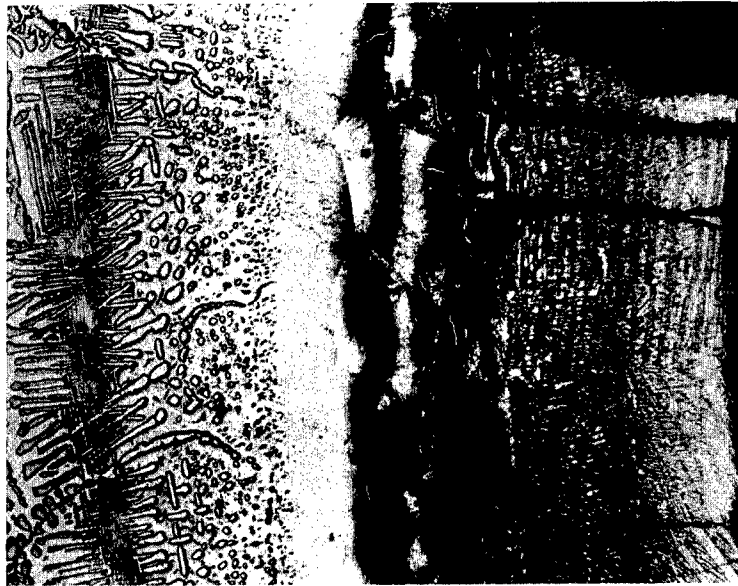
Fig. 11--Diffusion Bands of Carbide Formed by Heating Thorium in Contact With Graphite at 2105° to 2180°C for 22 Minutes, Furnace-Cooled, Air-Etched, X 90

Fig. 12--Typical Structure of ThC_2, Air-Etched, X 90

either side of the fine lamellar region gave values indicating only two phases. The fine lamellar region, however, gave hardness values which were higher than that obtained on the two phases existing on either side of it. The possibility of a third phase was suspected, but no confirming evidence for its existence was found. X-ray analyses of alloys with this structure gave evidence of only two phases, namely the metal and mono-carbide.

Figure 13 shows the structure of a sample heated between 1860 and 1880° C for 20 minutes in the same way and then quenched in oil. Although quenched, the dicarbide still exhibits a band structure similar to the dicarbide in the furnace-cooled sample. In between the dicarbide layer and the light area at the right is a dark one-phase area which appears to be a distinct band. This is believed to be due to the action of atmospheric moisture and that the dark one-phase region is a continuation of the lighter area. Figure 14 shows the same region etched with 1 nitric acid-2 ethyl alcohol-sodium fluosilicate solution. The boundary between the melt and the first diffusion band is clearly discernible. It is evident that partial precipitation still took place in the one-phase regions formed at the diffusion temperature.

Diffusion bands obtained at other temperatures in the range of 1750 to 2400° C gave no indications of any other one-phase regions.

Attempts to obtain diffusion bands between the metal and carbon at 1400° C and at 800° C by heating at these temperatures for 48 hours proved unsuccessful. The reason for this is believed to be due to the formation of an oxide film on the metal surface as well as due to a low rate of diffusion.

B. Determination of Liquidus Line

A series of alloys was prepared by heating thorium metal to temperatures above its melting point in graphite crucibles under vacuum. The center portion of each billet was analyzed for carbon content. The results obtained are given in Table II.

In most cases the melt was furnace-cooled to room temperature. Polished cross-sections of the samples showed no major segregation of the carbide first precipitated from the melt. This was further
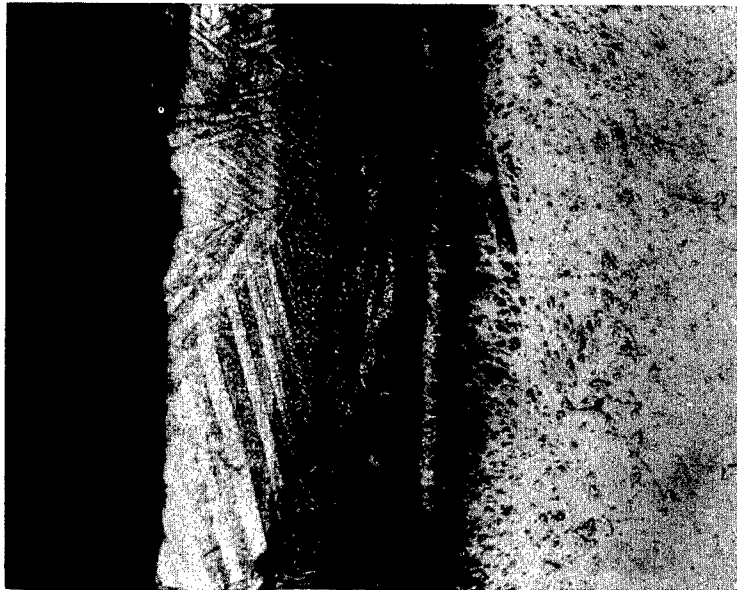
Fig. 13--Diffusion Bands of Carbide Formed by Heating Thorium in Contact With Graphite at 1860° to 1880°C for 30 Minutes, Oil-Quenched, Air-Etched, X 220

Fig. 14--Same Sample as Shown in Fig. 13, Etched With 1 Nitric Acid-2 Ethyl Alcohol-Sodium Fluosilicate Solution, X 90

Table II

Equilibrium Carbon Content of Thorium Heated in Contact
With Graphite

Sample No.	Temp. °C	Time at Temp. Minutes	Per Cent Carbon	Rockwell Hardness
1	1770-1825	29	0.3	73B
2	1825-1850	30	0.2	68B
3	1860-1880	20	0.3	...
4	1870-1970	20	0.6	91B
5	2105-2180	22	1.0	98B
6	2125-2205	17	1.0	97B
7	2150-2250	9	1.1	...
8	2350-2435	11	2.2	25C

checked by quenching two samples 3, and 7, from the temperature to which
they were heated. The carbon analyses obtained were found to be con-
sistent with the other data as given in Table II. These data then re-
present temperature-composition points on the liquidus line as shown in
Figure 10.

1. Microstructures of fused alloys

The microstructures of the central region of fused alloys prepared,
as described above, are shown in Figures 15 through 19. From Figure 15
it is evident that the solid solubility of carbon in thorium at room
temperature is appreciably less than 0.3%. The structures in Figures
15 and 16 of two alloys containing 0.3 and 0.6% carbon, respectively,
show no evidence of primary dendrites of carbide, the carbide present
being in the form of needles or plates scattered throughout the grains
and at the grain boundaries indicating precipitation from the solid
state. An alloy containing 1.0% carbon, Figure 17, shows areas of car-
bide in thorium-rich matrix. The same sample after etching, Figure 18,
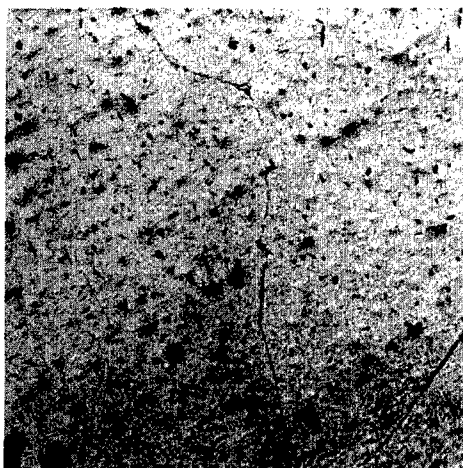shows evidence of precipitation in the solid state from both the car-

Fig. 15--Fused Sample, 0.3%
Carbon, From Center of Thorium
Billet Heated at 1770° to
1825°C for 19 Minutes in Con-
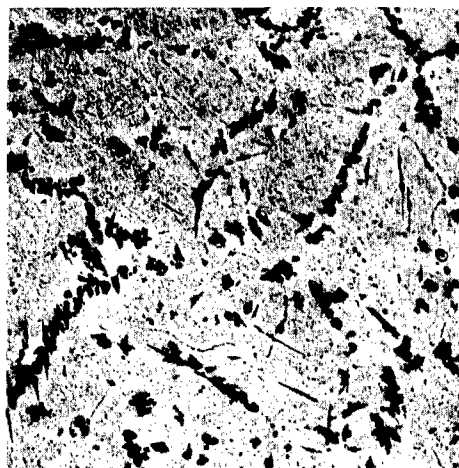tact With Graphite, Furnace-
Cooled, Unetched, X 100.

Fig. 16--Fused Sample, 0.6%
Carbon, From Center of Thorium
Billet Heated at 1870° to
1970°C for 20 Minutes in Con-
tact With Graphite, Furnace-
Cooled, Unetched, X 75.

Fig. 17--Fused Sample, 1.0%
Carbon, From Center of Thorium
Billet Heated at 2105° to
2180°C for 22 Minutes in Con-
tact With Graphite, Furnace-
Cooled, Unetched, X 250.

Fig. 18--Same Sample as Shown
in Fig. 17, Etched Electro-
lytically With 50:50 Ortho-
phosphoric and Glacial Acetic
Acid at a Current Density of
Approximately 1 Ampere Per
Square Inch, X 250.

bide-rich phase and the thorium phase, indicating appreciable decrease in mutual solid solubility of the two phases on cooling to room temperature.

The structure shown in Figure 19 of an alloy containing 2.2% carbon indicates coprecipitation of nearly equal amounts of thorium-rich and monocarbide-rich phases. The large light regions are interpreted as thorium-rich areas formed during solidification. This structure corresponds fairly well with the fine lamellar structure formed in the diffusion band shown in Figure 11.

C. Sintered Alloys

Alloys were also prepared by heating pressed powder compacts in graphite crucibles under vacuum in an induction furnace and then either quenching or slowly cooling to room temperature. The cooling rate was approximately the same as that described for the fused alloys. In the quenching experiments helium was introduced into the system, the vacuum head removed and the crucible was then removed and completely submerged in oil. Sintered or partially fused alloys were also obtained by passing a high electric current through pressed bars in the process of making melting point determinations. In most cases heating was carried out in a helium atmosphere and at the melting temperature the bars usually melted in two, the sample thus cooling rapidly to room temperature.

Sintered alloys containing 1.8 to about 3.8% carbon furnace-cooled to room temperature show varying degrees of precipitation of thorium or of the monocarbide phase as shown in Figures 20 and 21. Figure 20 shows monocarbide (dark phase) precipitating at the grain boundaries and within the grains, whereas Figure 21 shows thorium precipitating at the grain boundaries and within the grains. These structures may be explained on the basis of two solid solutions cooled slowly through opposite boundaries of an immiscibility gap as shown in Figure 10. Alloys containing 3.8 to 4.92% carbon are one-phase alloys at room temperature. A characteristic structure is shown in Figure 22. The black areas in this figure are principally voids.

Microstructures of compacts heated at about 1900° C for approximately 10 minutes and then quenched in oil show that the alloys containing from 4.92 to about 2.6% carbon are one-phase at this temperature, while alloys near 1% carbon appear to be two-phase (see Figures 23 and 24).
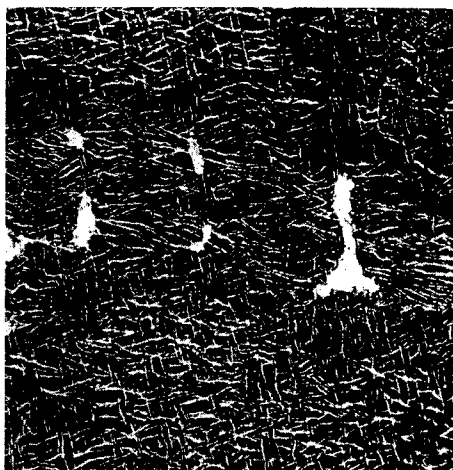
Fig. 19--Fused Sample, 2.2%
Carbon, From Center of Thorium
Billet Heated at 2350° to
2435°C for 11 Minutes in Con-
tract With Graphite, Furnace-
Cooled, Air-Etched, X 100.

Fig. 20--Sintered Alloy, 1.8%
Carbon, Heated at 1900°C for
3 Minutes, Furnace-Cooled,
Air-Etched, X 100.

Fig. 21--Sintered Alloy, 2.6%
Carbon, Heated at 1975°C for
3 Minutes, Furnace-Cooled,
Air-Etched, X 100.

Fig. 22--Sintered Alloy, 4.1%
Carbon, Heated at 2110°C for
10 Minutes, Furnace-Cooled,
Air-Etched, X 250.

The latter alloys have a coarse granular eutectoid-type structure which may have resulted from precipitation due to an insufficiently rapid cooling rate. The structures of alloys obtained as a result of melting point determinations give evidence that all alloys containing up to 4.92% carbon are one-phase at near their melting temperatures. Microstructures of many of these alloys show two-phases, but one of these phases evidently resulted from precipitation or decomposition in the solid state, indicating that the cooling rate was insufficiently rapid to hold the high temperature form (see Figures 25, 26, and 27). Figure 28 shows the structure of the 1.1% carbon alloy shown in Figure 25 after annealing at approximately 1800° C for five minutes and furnace-cooling to room temperature. A very large decrease in solid solubility is evident. The annealed structure resembles very closely that of a slowly cooled fused alloy of the same composition.

In the region between 4.92% carbon, composition of ThC, and 9.38% carbon, composition of ThC_2, the alloys cooled rapidly in helium from their melting temperatures show structures indicating that this is also a one-phase region at elevated temperatures (see Figures 29, 30, and 31). All alloys in this region are two phase alloys at room temperature. The two phases have been identified by X-ray analysis to be ThC and ThC_2. The lattice spacings correspond very closely to those for the pure compounds showing no appreciable mutual solid solubility. The temperatures at which these alloys change from one-phase to two-phase alloys have not been established. Attempts to hold the high temperature form by quenching proved unsuccessful. Figure 32 shows the structure of a sintered 7.2% carbon alloy slowly cooled to room temperature and Figure 33, the structure of an 8.0% carbon alloys after annealing at 1625° C for 60 minutes and rapidly cooling to room temperature in a helium atmosphere.

Thorium dicarbide and graphite form a eutectic at approximately 12.6% carbon melting at 2500 $\pm$ 35° C. This eutectic has been established from melting point determinations and the microstructure of alloys obtained. Pressed compacts corresponding to the composition of ThC_2 when heated in contact with graphite were observed to melt at between 2500 and 2535° C. The resulting eutectic structure formed is shown in Figure 34. Evidently the melting point of this eutectic was also observed by Prescott and Hincke (10) by a similar procedure but mistaken by them as the melting point of the dicarbide.
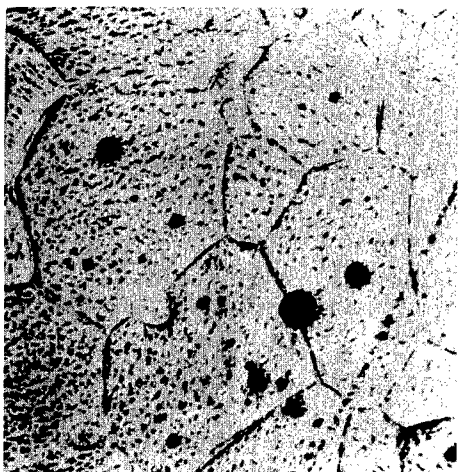
Fig. 23--Sintered Alloy, 2.6%
Carbon, Oil-Quenched From
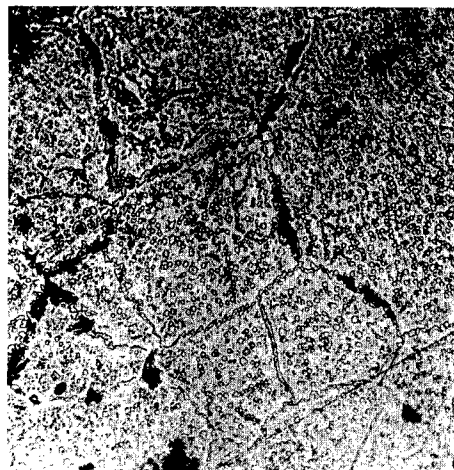1900°C, Unetched, X 250.

Fig. 24--Sintered Alloy, 1.0%
Carbon, Oil-Quenched From
1900°C, 1 Part Nitric Acid to
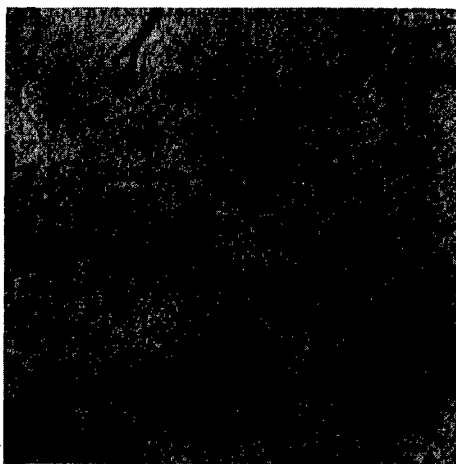2 Parts Methyl Alcohol Etch,
X 250.

Fig. 25--Sintered Alloy, 1.1%
Carbon, Cooled in Helium From
2010°C, Unetched.

Fig. 26--Sintered Alloy, 1.3%
Carbon, Cooled in Helium From
2025°C, 1 Part Nitric Acid to
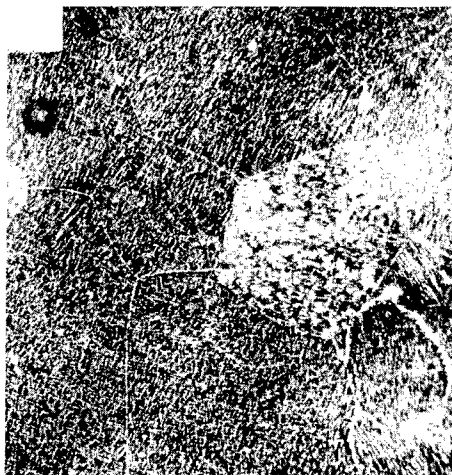2 Parts Methyl Alcohol Etch,
X 250.

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Fig. 27--Sintered Alloy, 2.1%
Carbon, Cooled in Helium From
2085°C, 1 Part Nitric Acid to
2 Parts Methyl Alcohol Etch,
X 250.

Fig. 28.--Same Sample as Shown
in Fig. 25, Annealed at 1800°C
for Approximately 5 Minutes
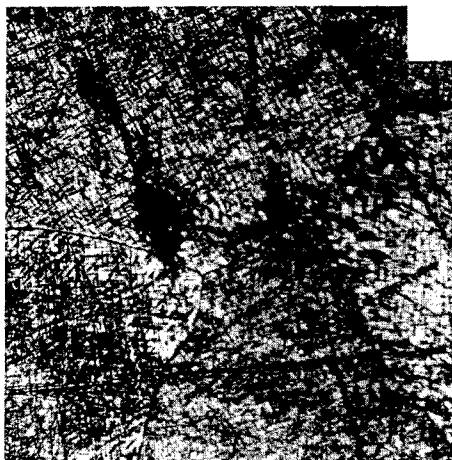and Furnace-Cooled to Room
Temperature, Unetched, X 250.

Fig. 29--Sintered Alloy, 5.1%
Carbon, Cooled in Helium From
2605°C, Air-Etched, X 250.

Fig. 30--Sintered Alloy, 6.1%
Carbon, Cooled in Helium From
2615°C, Air-Etched, X 250.

Fig. 31--Sintered Alloy, 8.0% Carbon, Cooled in Helium From 2655°C, Air-Etched, X 250.

Fig. 32--Sintered Alloy, 7.2% Carbon, Heated at 2400°C for 21 Minutes and Furnace-Cooled to Room Temperature, Air-Etched, X 250.
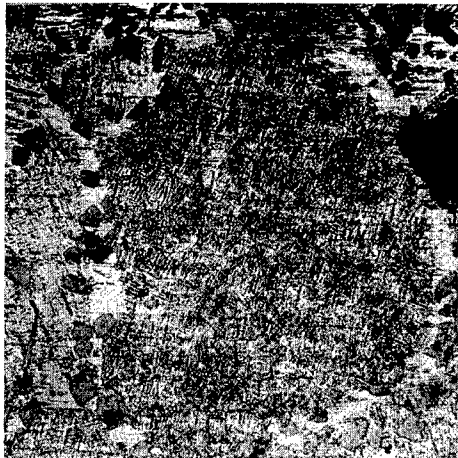

Fig. 33--Same Sample as Shown in Fig. 31, Annealed at 1625°C for 60 Minutes, Air-Etched, X 250.

Fig. 34--ThC_2-C Eutectic Containing Approximately 12.6% Carbon, Furnace-Cooled, Unetched, X 100.

D. Melting Points

Melting temperatures of thorium-carbon alloys were determined by Pirani and Alterthum's method as previously described. The results obtained are given in Table II.

A considerable variation in the melting point of the metal, containing 0.09% carbon, was observed as shown in Table III. This variation is believed to be due principally to contamination by small amounts of oxygen and nitrogen in the process of determining the melting point. The samples melting at 1695 and 1780° C were cold rolled from a thickness of approximately 0.25" to 0.35" and 0.073", respectively, before appreciable cracking along the edges of the samples took place. This showed that the lower melting sample was more ductile and therefore probably contained less impurities. To further check this point, the two rolled strips were annealed at 800° C for one hour and the electrical resistance and hardness compared. The metal with a melting point of 1695° C gave the lowest value for both of these properties. The best value for the melting point of the metal is therefore considered to be approximately 1695° C. Thompson (21) observed values for the melting point of electrolytic thorium ranging from 1672 to 1695° C and for calcium-reduced thorium values of 1712 to 1739° C.

The effect of nitride and oxide on the melting point of the metal is uncertain. Both the mononitride and the oxide have very high melting points. Norton (22) gives 3030° C as the melting point of pure thoria. Thorium mononitride melts with partial decomposition at approximately 2630° C (23). The variation in melting point determined by the above method may be due in part to the presence of oxide and nitride films at the grain boundaries or on exposed surfaces. These films unless dissolved by the metal would tend to prevent the metal from flowing into the small cavity in the bar, and the true melting point would not be observed. Relative to this point, Pietenpol and Miley (24) made some interesting studies on the effect of surface films on the temperature at which metal wires may be heated before they melt in two. In the case of lead they were able to heat a wire in air several hundred degrees above its melting point before the surface film ruptured.

In order to check the probable effect of oxide and nitride on the melting point of the metal, a number of tests were made on metal containing added ThO_2 and ThN.

Table III

Melting Points of Thorium-Carbon Alloys

Per Cent Carbon	Melting Point °C	Per Cent Carbon	Melting Point °C
0.09	1695	1.3	2025
0.09	1710		
0.09	1710	1.5	2140
0.09	1745		
0.09	1780	1.6	2165
0.24	1785	2.1	2200
		2.2	2245
0.35	1850		
0.35	1835	3.1	2455
0.46	1860	4.1	2560
0.59	1960	4.9	2625
0.59	1900	5.0	2620
0.59	1915	5.1	2605
0.59	1910	5.2	2605
0.59	1905		
		6.1	2615
0.71	1910		
0.71	1930	7.3	2635
0.85	1975	8.0	2655
0.85	1940		
0.85	2000	9.4	2655
0.85	1980	9.4	2660
0.96	2030	11.9	2545
1.1	1985	14.9	2500
1.1	2035		
1.1	2085		
1.1	2010		
1.1	2055		
1.1	2015		

Finely divided thoria, made by decomposing very pure thorium oxalate, was used in preparing Th-ThO$_2$ mixtures. The residual carbon content of the calcined oxalate was 0.064%. Eleven samples in which the added thoria content was varied from 0.25 to 50.0% all gave melting points in the range of 1740 to 1780° C. The sample containing 50.0% thoria was further heated, after the hole filled with melt, to 2520° C before the bar melted in two. At this temperature a large center portion of the bar fell to the cold furnace base. X-ray analysis of the sample quenched in this manner showed only two phases present, ThO$_2$ with a$_0$ = 5.59 Å and thorium with a$_0$ = 5.10 Å. It may be concluded, therefore, that the solid solubility between the metal and the oxide is small even at very high temperatures. Microstructures also indicate very little solid solubility.

The nitride used in preparing Th-ThN mixtures was obtained by passing ammonia over the powdered metal at approximately 900° C. The product obtained had a rather light maroon color and a nitrogen content corresponding approximately to the formula ThN$_{1.2}$. Nine samples in which the ThN content, added as ThN$_{1.2}$, was varied from 0.6 to 25.3% all melted in the range of 1770 to 1855° C. With 31 and 60% ThN, the observed melting points were 1905 and 2185° C, respectively. Another sample containing 64% ThN was heated to 2345° C before the hole filled with melt. At this temperature a large section of the bar fell to the water-cooled furnace base. The quenched material gave an X-ray powder diffraction pattern showing two face-centered cubic phases. These were identified as thorium with a$_0$ = 5.14 Å and thorium mononitride phase with a$_0$ = 5.18 Å. A microstructure of this sample revealed that the initial nitride added had not been completely dissolved. The total heating time for this test bar at above 1600° C was approximately 42 minutes. A longer heating period might have resulted in a higher degree of solubility between the nitride and the metal. Microstructures further indicate a rapid decrease in solid solubility with decrease in temperature. The undissolved nitride is readily detected as a bright golden yellow phase in the microstructure.

It is evident from these observations that both the nitirde and oxide increase the observed melting temperature of the metal.

Another factor which may be considered to contribute to variations in the observed melting temperatures of alloys is the reaction between the carbide and oxide initially present in the metal. At temperatures of 1900° C or above, part of the carbon added is lost as carbon

monoxide. No attempt was made to correct the observed results for loss of carbon due to this reaction. Furthermore, the pressed compacts remain quite porous up to the melting temperature, and the first melt does not necessarily flow or concentrate in the small hole drilled in the bar with the result that the observed melting temperature may be expected to be higher than the corresponding solidus temperature.

The results obtained are plotted in Figure 10. Two melting point maxima were obtained at 4.92 and 9.39% carbon, corresponding to the composition of ThC and ThC_2.

E. X-ray Analyses

Alloys prepared by powder metallurgy methods in which sufficient carbon was added to give a composition of 4.92% carbon, the composition of ThC, gave X-ray powder diffraction patterns corresponding to a sodium chloride-type structure with a lattice constant of 5.34 Å. X-ray studies of furnace-cooled alloys showed the lattice of this phase to vary from 5.29 to 5.34 Å, confirming the wide solid solubility range of thorium in the monocarbide as observed metallographically. Alloys quenched in a helium atmosphere from their melting temperatures, or oil-quenched from 1900° C, did not show a continuous change in the lattice constant. The largest lattice constant measured for a metal-carbon solid solution was 5.15 Å and the smallest lattice constant for a monocarbide-metal solid solution was 5.26 Å. Microstructures, however, indicate complete solid miscibility between the metal and thorium at elevated temperatures.

A well annealed alloy containing 7.3% carbon showed two phases to be present, the monocarbide with $a_o \cong 5.34$ Å and the dicarbide. The X-ray spacings for the dicarbide were in very close agreement with those observed for samples containing 9.38% carbon, the composition of the dicarbide. It may therefore be concluded that there is little mutual solid solubility between these two compounds at room temperature.

Since microstructures show that the monocarbide and the dicarbide form a complete series of solid solutions at high temperatures, it was assumed that the dicarbide probably transforms from a cubic structure to a pseudo tetragonal structure on cooling to room temperature. In an attempt to hold the high temperature form, a molten sample containing excess graphite was quenched in oil from 2700° C. The quenched sample

gave a diffraction pattern corresponding closely to that of the com-pound furnace cooled to room temperature. A few extra lines identified as graphite maxima were also observed. It may be concluded from this evidence that the dicarbide either transforms very rapidly or retains its room temperature form at very high temperatures, also that the dicar-bide holds little or no graphite in solid solution on cooling to room temperature.

An X-ray powder diffraction pattern of the dicarbide taken at 600° C in a high temperature camera also showed no change in structure.

Single crystals of dicarbide were prepared by heating metal in a graphite crucible at 2400 to 2450° C for approximately four hours. Microscopic examination of a cross-section of the billet obtained showed the outer layer next to the graphite to be made up of very large grains of dicarbide. The center portion was one phase which was assumed to be monocarbide. The intermediate region had a Widmanstatter structure. Fragments could be readily broken from the outer portion of the dicarbide grains. Small pieces broken from these grains were placed in mineral oil to prevent decomposition by moisture and given to E. Hunt of the Ames Laboratory for X-ray single-crystal studies.

On the basis of single crystal X-ray diffraction patterns and neutron powder diffraction data Hunt (25) has been successful in working out the complete structure for the dicarbide. The compound was shown to have monoclinic symmetry. The lattice constants are $a_0 = 6.53$ Å, $b_0 = 4.24$ Å, $c_0 = 6.56$ Å, and $\beta = 104$. The calculated density, on the basis of four molecules per unit cell is 9.6 gms/cc.

Since X-ray analyses show the dicarbide to be one-phase, the peculiar microstructure, Figure 12, of the dicarbide is believed to be due to a high degree of twinning. The possibility of partial decomposi-tion of the compound was considered, but this could not be confirmed by X-ray analyses. If decomposition takes place, it is of insufficient extent to be detected by X-ray powder methods.

F. Resistance Measurements

The purpose of these measurements was to determine the temperature dependence of the electrical resistance of thorium and thorium-carbon alloys and to observe any discontinuities which might be interpreted as phase transitions or phase boundaries. With the exception of a number

of tests on massive thorium all other measurements were made on test bars
prepared by powder metallurgy methods. The test bars were given an
homogenizing anneal of about one hour at near their melting point before
readings were taken. Even after this treatment the test bars remain quite
porous and it was not possible to calculate the specific resistivity of
these alloys.

Temperature measurements were taken with an optical pyrometer. The
pyrometer was focused on a small hole in the center of the test bar as
previously described. Temperatures below 760° were extrapolated from a
plot of the temperature of a chromel-alumel thermocouple junction located
near but not in contact with the test piece, versus optical pyrometer
readings. This method was also used to extrapolate between
optical pyrometer readings at temperatures above 760° C when automatic
recording and control instruments were used. As many readings as possible
were taken with the optical pyrometer and extrapolations were made only
over periods of time, when it was necessary to leave the apparatus.

The results of resistance measurements on a 5/16" diameter by
4.0" thorium rod are given in Figure 35. These measurements were made
with the manually operated apparatus described on page 20. All tempera-
ture readings above 760° were taken with an optical pyrometer. The
average heating and cooling rate was approximately 4.0° C per minute.
The distance between the potential contacts on the test piece was
approximately 1.2 cm.

The curves obtained show a sharp increase in slope at approximately
1425° C. The sharp increase in resistance with temperature continues
to about 1525° C. The total heating time in this range of temperature
was approximately one hour. This break may be interpreted as a trans-
formation which takes place over a range of temperature either due to
too rapid a heating rate or due to impurities in the metal or both.

Above 1525° C the results obtained are erratic. The first heating
run gave indication of a fairly sharp rise in resistance at about 1700° C.
This was interpreted to be due to incipient fusion. The test piece was
held at this temperature for approximately 10 minutes. The resistance
gradually increased, but the hole did not fill with melt. The cooling
curve and the second heating curve followed the first heating curve
quite closely at temperatures below 1575° C. The second heating curve
shows a continued rapid increase in resistance at 1550 to about 1650° C.
This may have been due to a slight shift of the potential contacts due
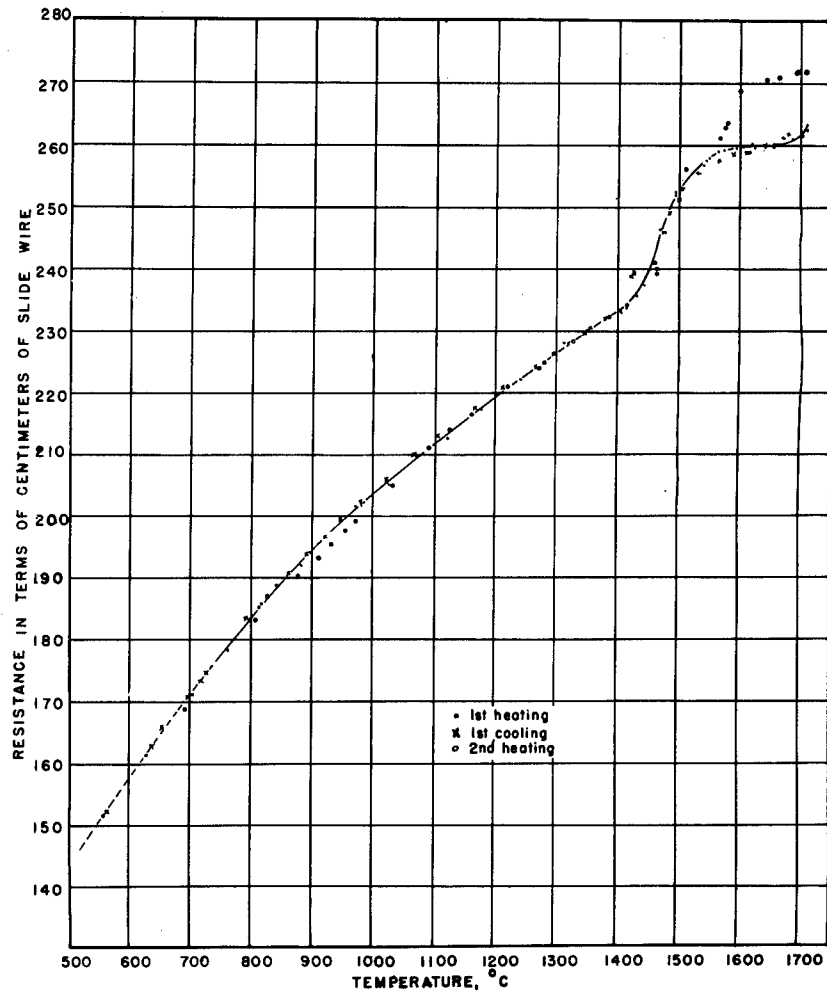to softening of the contact points. The test rod melted in two at

Fig. 35--Temperature Dependence of the Electrical
Resistance of Thorium.

approximately 1740° C. There was no indication of a rapid increase in resistance as this temperature was approached, as might be expected if this were the true melting point. This was also true of other thorium test bars for which the observed melting temperatures were above 1700° C. The possibility that the break at 1425° C represents the true melting point of the metal is questionable, although test bars heated to only 1550° C showed evidence of sagging under their own weight indicating that the resistance to shear is small at temperatures well below the observed melting point.

At near 1400° C some volatile impurities are given off by the metal. The possibility that volatilization of these impurities results in expansion of the metal and thus gives rise to the increase in resistance was also considered. However, no permanent expansion of the test bars was observed. Furthermore, this break was still observed after heating a test bar at 1500° C under vacuum for approximately one hour.

Similar runs on sintered metal bars, bars cut from cast metal, and on Westinghouse metal all gave a sharp increase in resistance at $1400 \pm 25^\circ$ C. Minor changes in slope were also observed in the temperature range of 700 to 950° C.

Attempts to correlate thermal breaks with the resistance breaks were not very successful. A cooling curve, obtained by means of a columbium-tungsten thermocouple, on a 450 gram sample heated to 1750° C in a beryllia crucible gave a weak indication of a thermal arrest between 1575 and 1610° C and a fairly well pronounced break at about 1430° C. A second run made in the same way showed a fairly strong break at 1690° C on heating and a fairly strong break at about 1300° C on cooling. No definite cooling break could be observed at 1690° C. Other cooling curves gave weak indications of breaks varying from about 1180 to 1400° C. The possibility of reaction between the metal and the beryllia crucible and contamination of the sample by both oxide and beryllium added further uncertainty to the results obtained, and no further work was done on thermal analyses.

Pressed bars containing as little as 0.2% carbon no longer gave a sharp increase in resistance at near 1400° C. Test bars containing 5 to 10% of added ThO_2 gave very erratic curves.

The results obtained on thorium-carbon compositions are given in

Figure 36. The dicarbide exhibits a sharp change in slope at about 1350 to 1650° C. The monocarbide shows a rather large hysteresis at 700 to 900° C. An X-ray diffraction pattern of the monocarbide quenched from 950° C gave no indication of a change from the room temperature structure.

A test piece containing 1.5% carbon gave a very sharp rise in resistance at 1670° C. This same sample was rapidly cooled in a helium atmosphere from approximately 1960° C and then annealed at 1690° C for 4.5 hours and again rapidly cooled to room temperature. The change in microstructure from the center of the test bar where the annealing temperature was 1690° C to near the end of the test bar where the temperature during annealing was probably below 1200° C. is shown in Figure 37. From these structures it is evident that at 1690° C the alloy is one-phase and that there is a rapid decrease in solid solubility below this temperature. The structure observed along the length of the bar also shows that there is no intervening one-phase region between 1690° C and near room temperature. The break at 1690° C may be the result of a change in structure of one of the components resulting in a large increase in solid solubility.

A similar sharp increase in resistance was obtained at 2025° C with a test bar containing 2.0% carbon.

In general, the results of resistance measurements indicate that the thorium-carbon system is more complex than shown in Figure 10. However, the data obtained are not sufficiently conclusive to justify changing the tentative diagram given. Further data are needed in order to properly interpret the results of these measurements. High temperature X-ray studies would be particularly useful in this respect.

In the course of these measurements it was noted that the dicarbide is a particularly good conductor of electricity at room temperature. The monocarbide, however, has a relatively high resistance, it being higher than the dicarbide by a factor of about five.
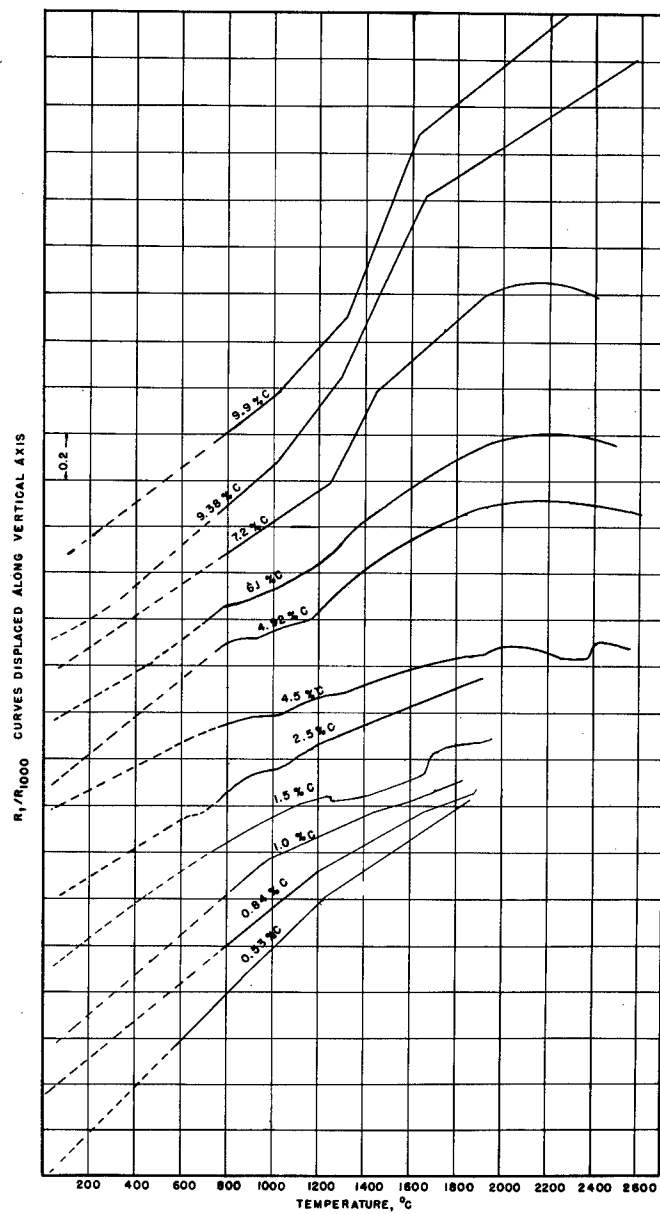
Fig. 36--Temperature Dependence of the Electrical
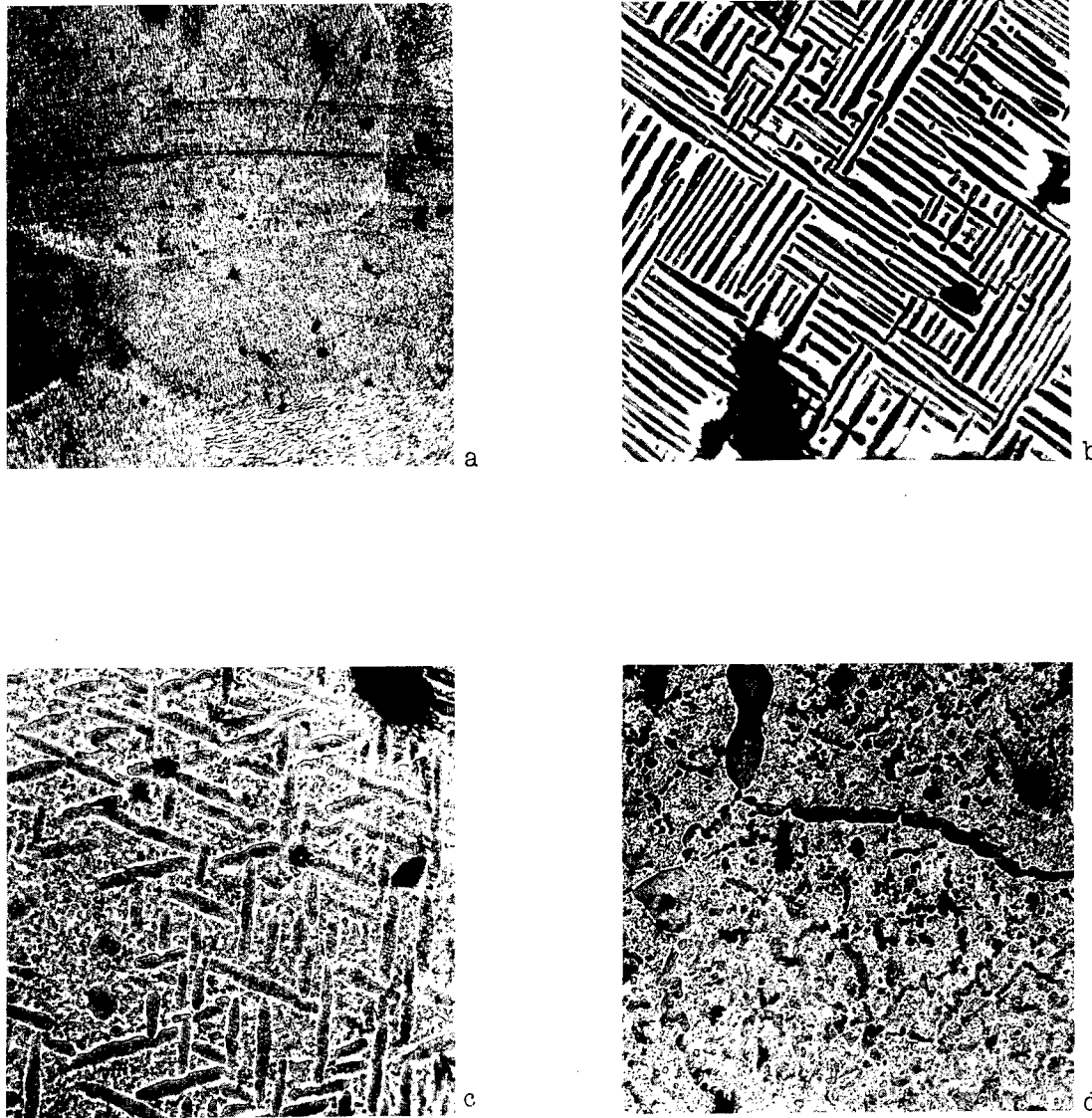Resistance of Thorium-Carbon Alloys.

Fig. 37--Microstructures of a 1.5% Carbon Test Bar Annealed at
1690°C for 4.5 Hours and Then Rapidly Cooled in a Helium Atmosphere
to Room Temperature. The Microstructure at the Upper Left is That
of the Center of the Bar, and Figures from Left to Right Show
Microstructures Taken Along the Bar Between the Midpoint and the
Water-Cooled Copper Electrode at Points of Successively Decreasing
Temperatures. Etched with 1 Nitric Acid - 2 Ethyl Alcohol - Sodium
Fluosilicate Solution, X 250.

VII. SUMMARY

A study of the thorium-carbon system has been made and a tentative phase diagram constructed from metallographic, X-ray, and melting point data.

The existence of two compounds, ThC (4.92% carbon) and ThC_2 (9.38% carbon), has been verified. No conclusive evidence for any other compound was found. The monocarbide has a sodium chloride-type structure and the lattice constant for this compound is shown to be 5.34 Å which is considerably larger than that previously reported. It is shown that the lattice constant previously measured was that of a solid solution of thorium in thorium monocarbide.

The monocarbide melts at 2625 ± 25° C and the dicarbide at 2655 ± 25° C. All compositions between thorium and the monocarbide show complete miscibility in the liquid state and in the solid state at elevated temperatures. However, an immiscibility gap in the solid solution area appears to extend from room temperature to just under the solidus line. The peak of this gap is at about 2% carbon and 1975° C. The composition of the thorium-rich and the carbon-rich solid solutions for this gap at room temperature are about 0.25% carbon and 3.8% carbon, respectively. The monocarbide and dicarbide also form a complete series of solid solutions at elevated temperatures but show very little or no mutual solid solubility at room temperature.

The dicarbide forms a eutectic with graphite containing approximately 12.6% carbon which melts at 2500 ± 35° C.

A method for the measurement of the electrical resistance of metals and alloys at very high temperatures is given and automatic recording and control instruments used in conjunction with this method have been described. This is essentially a potentiometer method wherein the potential developed between two probes which make contact with the test piece is balanced against the potential developed across the secondary of a current transformer whose primary is connected in series with the test piece. The test piece is mounted between water-cooled copper electrodes and is heated by means of a high 60 cycle current. The change in resistance is measured directly.

The temperature dependence of the electrical resistance of thorium and of a number of thorium-carbon compositions have been determined. Evidence indicating the existence of an allotropic modification of thorium at temperatures above 1400° C is presented. Part of the material presented in this paper has been previously published (26), (27).

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IX. ACKNOWLEDGMENTS

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